UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF ENFORCEMENT

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MULTI-MEDIA COMPLIANCE INVESTIGATION
(Volume 1 - Media Reports)

SHELL OIL COMPANY
Wood River Manufacturing Complex
Roxana, Illinois

April 1994

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Anne Bevington
Willis Collins
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EXECUTIVE SUMMARY

INTRODUCTION

At the request of EPA Region 5, the National Enforcement Investigations Center (NEIC) conducted a multi-media compliance investigation of the Shell Oil Company - Wood River Manufacturing Complex (Shell) located in Roxana, Illinois. Shell is located approximately 15 miles northwest of St. Louis, Missouri.

The refinery processes about 250,000 barrels of crude oil per day and produces motor gasoline, jet fuel, asphalt, benzene, hydrocarbon based solvent, heating oils, sulfur, propane, and lubricating oils. The refinery employs about 1,300 people on approximately 2,000 acres, and has operated at the present site since 1920.

OBJECTIVE

The specific objective of the investigation was to determine compliance with:

- Clean Air Act (CAA) regulations, including the National Emission Standards for Hazardous Air Pollutants (NESHAPs), New Source Performance Standards (NSPS), and the Illinois Administrative Code Title 35 - Air Quality Standards
- Clean Water Act (CWA) regulations, including National Pollutant Discharge Elimination System (NPDES) permit (IL0000205) requirements and Spill Prevention Control and Countermeasures (SPCC) regulations, and laboratory operating requirements
- Underground Injection Control (UIC) regulations under the Safe Drinking Water Act (SDWA)
- Resource Conservation and Recovery Act (RCRA) hazardous waste management regulations, including Land Disposal Restriction (LDR) requirements

- Underground Storage Tank (UST) requirements
- Emergency Planning and Community Right-to-Know Act (EPCRA) regulations, including Designation, Reportable Quantities and Notification requirements of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA § 103)
- Toxic Substances Control Act (TSCA) regulations for polychlorinated biphenyl (PCB) management

In addition, NEIC personnel identified refinery activities that, although not specifically regulated, could impact the environment.

INVESTIGATION METHODS

The investigation of Shell included:

- A review of federal and state regulatory files and databases
- An on-site inspection of the refinery conducted October 25 through November 5, 1993 that involved:
  - Discussions with refinery personnel including a detailed process description review
  - Review of refinery operations
  - Facility records/document review
  - Collection of samples from various process areas
- An on-site monitoring inspection of components in volatile organic compound (VOC) service conducted November 15 through 19, 1993.
- An audit of the on-site environmental testing laboratory
- Exit conferences between regulatory and refinery personnel to discuss preliminary inspection findings. NEIC personnel stressed that the final determinations will be made in conjunction with regional and state personnel.

BACKGROUND

Refinery operations include atmospheric and vacuum distillation, catalytic cracking, hydrocracking, hydrotreating, catalytic reforming, alkylation, lube oil manufacturing, sulfur recovery, and asphalt plants. Products may be stored prior to shipment by railcars, barge, and truck.

A process description, including discussion of waste streams generated, is presented in the "Process Description/Waste Generation" section of this report.

Pollution prevention activities/environmental accomplishments of the Shell refinery and potential pollution prevention opportunities are discussed in the "Pollution Prevention" section of this report.

The major sources of air emissions at Shell are refinery fuel gas/oil/pitch fired boilers and heaters, two catalytic cracking units, product storage tanks, sulfur recovery units, flares, and fugitive losses. Air emissions from the refinery are regulated by 35 operating permits issued by Illinois Environmental Protection Agency (IEPA). Several of the permits regulate process units constructed/modified in the 1970s subject to NSPS, 40 CFR Part 60.

Asbestos and benzene are regulated NESHAP, 40 CFR Part 61, compounds present at the refinery. Asbestos removal projects are ongoing and generally conducted by contractors. Shell has established a leak detection and repair (LDAR) program for 2,600 components in benzene service subject to NESHAP, and 1,300 VOC components subject to NSPS.

Fugitive VOC emissions occur from approximately 50,000 components (valves, pumps, and compressors) in VOC service. The facility has established an LDAR program to monitor for VOC leaks.

Shell discharges over 6 million gallons per day of wastewater under NPDES Permit Number IL0000205 to the Mississippi River. The NPDES permit, effective August 5, 1993, regulates two wastewater, and eight stormwater outfalls. Wastewater treatment includes screening, neutralization, oil/water separation, dissolved air flotation, activated sludge, secondary clarification, and polishing in lagoons. Treated effluent from the Village of Roxana's sewage treatment plant is sent to Shell's polishing lagoons and discharged through one refinery outfall.

Shell uses well water for plant process water and the Village of Roxana municipal water supply for drinking water. Sanitary wastes are mixed with process wastewater and discharged to the on-site wastewater treatment plant. Thirty-four septic/sanitary systems are operated at the refinery.

The refinery (EPA ID number ILD080012305) generates, stores, and treats hazardous waste. A RCRA permit was issued November 3, 1989 for storage of hazardous waste in containers. On March 22, 1991, Shell modified the RCRA Part B permit application to include four tanks for storage of hazardous waste and two surface impoundments for treatment of hazardous waste. This modification also addressed the closure of a solid waste disposal basin. In February 1993, a revision to the RCRA Part B permit application added one tank to replace the four tanks added in the March 1991 revision. The four tanks are undergoing closure. In September 1993, the closure plans for the two surface impoundments were updated to allow both impoundments to operate as nonhazardous waste impoundments after March 1994.

The IEPA has filed two RCRA complaints against Shell. The first complaint includes violations that resulted from the storage of refractory brick containing lead for longer than 90 days. The second complaint includes violations resulting from the disposal of lime sludge filter cake containing benzene at a non-RCRA off-site facility. Settlements for both complaints are being negotiated by IEPA and Shell.

Shell removed 10 USTs from service in November 1989, and 1 in February 1991. The tanks were closed and no visual evidence of tank deterioration, leakage, or evidence of soil contamination was found. No USTs are currently in service at Shell.

Pursuant to EPCRA, Shell reported that approximately 900,000 pounds (total) of chemicals were released from the refinery during 1992. A partial listing of released chemicals includes:

- ammonia
- 1,3-butadiene
- benzene
- chlorine
- cobalt
- creosol
- chromium compounds
- cumene
- cyclohexane
- diethanolamine
- ethylbenzene
- ethylene
- methyl tert-butyl ether
- molybdenum trioxide
- naphthalene
- phenol
- propylene
- sulfuric acid
- toluene
- 1,2,4-trimethylbenzene
- xylene
- zinc compounds

PCB transformers and PCB capacitors have not been in service at the refinery since January 1991. No known PCB or PCB-contaminated equipment is operated at Shell.

Shell operates analytical equipment and laboratories to monitor compliance with several regulations. Shell reports data relating to wastewater discharges regulated under NPDES; monitors sulfur levels in refinery pitch used as fuel in heaters; and has monitored benzene levels in wastewater as required by 40 CFR Part 61 Subpart FF. Analysis of hazardous waste samples are conducted by an outside laboratory.

SUMMARY OF FINDINGS

The areas of noncompliance and areas of concern,* based on inspection observations, discussions with Shell personnel, and review of documentation, are summarized below. Details of these findings are discussed in separate media sections of this report.

POLLUTION PREVENTION

While Shell has undertaken some pollution prevention activities, other opportunities were identified by NEIC. For example, numerous opportunities exist for the reduction of fugitive volatile organic compounds emissions through modifications of the Leak Detection and Repair Program. Discontinuing the use of chromium in the treatment of cooling tower waters will decrease the amount of hazardous waste generated and reduce chromium air emissions.

CLEAN AIR ACT

The following areas of noncompliance and areas of concern of the air pollution control requirements were identified during the investigation.

Areas of Noncompliance

40 CFR § 60.40(c)	When fired with refinery fuel pitch, boiler No. 17 is not operated in accordance with NSPS requirements. Inappropriate monitoring and recordkeeping are maintained.

* *Areas of concern are inspection observations of potential problems that could result in noncompliance with permit or regulatory requirements, or are areas associated with pollution prevention issues.*

35 IAC Section 215.144(d)	On five occasions, the number of excessive organic releases from safety relief valves has exceeded three in a 12-month period.
40 CFR § 61.243-1, as referenced by 40 CFR § 61.112 (b)	Shell exceeded the 2% allowable for valves leaking under the alternative monitoring standard. NEIC identified four units in Benzene NESHAP service with leak rates greater than 2% including: - Benzene Extraction Unit - Catalytic Reformer-1 - Catalytic Reformer-3 - Dispatching
40 CFR § 60.483-1, as referenced by 40 CFR § 60.592 (b)	Shell exceeded the 2% allowable for valves leaking under the NSPS alternative monitoring standard. NEIC determined a leak rate greater than 2% at the Catalytic Dewaxing Unit.
40 CFR § 61.242-6	Plugs, caps, blind flanges, or secondary valves were missing from two benzene NESHAP unit valves with tag numbers A-000256 and A-000258.
40 CFR § 61.242-1(d)	Five valves in the benzene extraction unit were not marked in a manner to distinguish them from other equipment. Three valves near tag number A-000239 were not tagged, and two duplicate tag numbers (C-000231 and B-000011) were used.

35 IAC Section 212.123	Excess emission reports from January 1, 1991 through October 1993 were reviewed and the 30% opacity limits for catalytic cracking unit (CCU) -1 and CCU-2 were exceeded. CCU-1 opacity was between 30 and 60% during 19 6-minute periods and exceeded the 60% limit during 4 6-minute periods. CCU-2 opacity was between 30 and 60% during 30 6-minute periods and exceeded 60% during 55 6-minute periods.
40 CFR § 60.42 (a)(2)	Boiler No. 17 opacity exceeded the maximum allowable limit of 27%. This limit was exceeded on 30 6-minute periods, during the third quarter of 1993.

Areas of Concern

- There is no emission monitoring of the CCU bypass stacks. When the CO boiler and/or ESP is down for maintenance or during an upset condition, the exhaust gases are vented directly to the auxiliary stack. Significant emissions are released through these stacks during bypass events.

- The CCU stack test may not accurately reflect the emission rates from the CCU-1 and CCU-2. Soot blowing activities were curtailed during the stack tests.

- The H_2S fuel content for vacuum flasher heaters 1 and 2, the catalytic dewaxer heater, and boiler 18 (NSPS units) is not monitored when natural gas is burned, These units are connected to both the refinery fuel gas (RFG) and natural gas supply systems. The RFG supply line has been blocked (not removed) and only natural gas is exclusively routed to the heaters. RFG H_2S content is continuously monitored;

however, the natural gas H_2S content is not monitored. Shell should be required to clearly report when fuel types are changed.

- Remediation groundwater used in the refinery is contaminated with benzene and is a significant source of benzene emissions. The benzene in the extracted groundwater does not need to be included in the TAB, however, the water streams containing more than 10 parts per million (ppm) benzene must be controlled in accordance with Subpart FF. Benzene control measures for the well water streams containing greater than 10 ppm benzene were not included in the Application for Waiver of Compliance.

- The VOC component leak rate determined by NEIC was greater than the leak rate reported by Shell for six units inspected. The NEIC and Shell leak rates for monitored units are summarized below:

Process Unit	NEIC Leak Rate %	Shell Leak Rate %
Benzene Extraction	7.8	0.8
Catalytic Reformer-1	6.1	0.8
Catalytic Reformer-3	7.3	1.5
Dispatching	3.9	0.0
Catalytic Dewaxing	7.2	0.4
Deasphalting	1.0	0.2

- Missing or loosely fitting plugs at the end of open-ended valves were the source of several VOC leaks. Secondary closure devices such as caps, blind flanges, plugs, or second valves are only required for NSPS and NESHAP regulated portions of the facility. Most refinery portions are not covered by these requirements.

- Jurgason valves on reactor level gauges are a source of fugitive VOC emissions. Shell is inconsistent in monitoring these valves. Jurgason

valves are included in the monitoring program at some process units and not at others. Other valves on the level gauges are tagged and monitored. NEIC identified several Jurgason valves that were not uniquely identified and were leaking, including two valves at the catalytic dewaxing unit on the level gauge for vessel 4728 and two valves on vessel 1803 at the deasphalting unit.

- Motorized valves (MOVs) are a significant source of fugitive VOC emissions. Ten MOVs on the catalytic reformer (CR) -1 reactors, and eight MOVs on the CR-3 reactors were found leaking. At least one MOV on the top of Reactor D at CR-1 was a source of significant VOCs. Hydrocarbons could be seen leaking from the Reactor D MOV and the OVA <u>background</u> reading was in excess of 1,000 ppm.

- Shell instrument calibration procedures do not meet the requirements outlined in Method 21. The TLV monitor is calibrated using a zero span gas and 3,000 ppm hexane instead of the 10,000 ppm leak standard value required in Method 21. Shell correspondence to Region 5 on April 23, 1990 requested the use of 3,000 ppm hexane for the calibration procedures. Shell provided the Region with data indicating response of the TLV is adequate using 3,000 ppm hexane for calibration. Region 5 responded on May 15, 1990 allowing Shell to use an alternate calibration gas of 3,000 ppm. Using a calibration gas lower than the leak standard may affect the accuracy of the instrument for readings greater than 3,000 ppm.

- The refinery will need to improve the VOC program in order to comply with the 2% alternative standard requirements. In order to comply with the requirements, the refinery may need to replace some of the older valves with newer technology.

- Inconsistencies exist within Permit No. 72110620 (WRR-6) in limiting H_2S concentration in the fuel gas used in the vacuum flasher process heaters. Condition 1b specifies an H_2S limit of 0.1 grains per dry standard cubic feet (gr/dscf) and condition 6b identifies a 39 gr/100 dscf limit. Clarification of the permit should be considered to eliminate possible confusion in the conflicting requirements of conditions 1b and 6b.

- Emission of approximately 170,000 pounds of ammonia from CCU-1 and CCU-2 is unregulated. The permits for the CCU-1 and CCU-2 allow ammonia injection for conditioning during start-up of the electrostatic precipitator (ESP). Discussions with refinery personnel indicated that ammonia is injected to extend the maintenance cycle of the ESP, not during start-up.

- Compliance with the individual source operating group (SOG) SO_2 limits cannot be determined from the information provided on the Shell quarterly SO_2 reports. The reports list only daily totals and compliance is based on a 3-hour block average. Shell maintains records for hourly and 3-hour block average SO_2 limits, as required in the permits, but this information is not provided or required on the quarterly reports.

- The 1,000 ppm SO_2 limit for the sulfur recovery unit emissions was exceeded on 28 occasions. Several of these excess emissions due to upsets, malfunction, or breakdowns resulted in releases of tons of SO_2. Operating and maintenance practices should be reviewed to minimize these excess emissions.

- The 39 H_2S gr/100 dscf Illinois Administrative Code (IAC) limit for the refinery fuel gas (RFG) limit was exceeded on 22 occasions from January

1991 through October 1993. Permit provisions of the affected process units allow the IAC limit of 39 H_2S gr/100 dscf limit to be exceeded.

CLEAN WATER ACT - NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM

The following areas of noncompliance and areas of concern of the water pollution control requirements were identified.

Areas of Noncompliance

35 IAC § 304.106	Visible oil was discharged to Grassy Lake on April 25, 1993.
NPDES Permit IL0000205 Special Condition 18	Shell is not conducting influent monitoring at the location required by permit. An alternate location has been used without IEPA authorization.
NPDES Permit IL0000205 Effluent Monitoring Standard Condition 10(a)	Shell has not conducted proper effluent monitoring of outfall 001, as specified by the NPDES permit when high river levels disable the 001 flow meter.
NPDES Permit IL0000205 Effluent Limitations Outfall 001	Outfall 001 discharge monitoring reports (DMRs) document one daily maximum biochemical oxygen demand (BOD) load exceedance, two daily maximum BOD concentration exceedances, and one monthly average BOD concentration exceedance during the period of January 1991 through September 1993.
NPDES Permit IL0000205 Effluent Limitations Outfall 002	Outfall 002 DMRs document one daily maximum chloride concentration exceedance during the period of January 1991 through September 1993.

NPDES Permit IL0000205 Effluent Limitations Outfall 003	Outfall 003 DMRs document two pH exceedances during the period of January 1991 through September 1993.
NPDES Permit IL0000205 Standard Condition 5	Shell did not maintain adequate laboratory controls or appropriate quality assurance procedures including: incomplete chain-of-custody procedures, daily calibration checks were not performed, and method blanks not completed.

Areas of Concern

- Due to decreased capacity from material deposition, Shell's stormwater detention area has the potential to overflow and impact Grassy Lake. The detention area appears to be filling with sediment, reducing its capacity. According to Jay Rankin, Senior Engineer, the detention area was probably constructed in the 1940s and has not been dredged to his knowledge. The detention area overflowed into a roadside ditch along Route 111 on April 25, 1993 after a 3-inch storm event. Oil was washed out of the detention area and flowed with the water in the ditch to outfall 003. The oil was discharged to Grassy Lake causing a sheen. Outfall 003 was sampled three times per day for 4 days. No exceedances of the NPDES limits for oil and grease (30 mg/L) were reported.

- Shell cannot accurately measure effluent flow through outfall 002. Outfall 002 includes effluent from the two secondary clarifiers and the secondary sludge thickener. Each clarifier has two magnetic meters for flow measurement: one on the influent to the clarifier and one on the recycle line to Pond 2. Shell determines the clarifier effluent flow to outfall 002 by taking the difference between the two flow meter measurements for each clarifier. This measurement will be biased high

because there is no consideration for flow wasted to the sludge thickener. Flow from the sludge thickener to outfall 002 is determined by a flow meter on the sludge thickener influent line. This measurement is biased high because there is no consideration for flow sent to the solids dewatering facility.

- Shell does not accurately monitor the effluent for outfall 002 NPDES compliance. A composite sampler is installed to sample the clarifier effluent, but does not include the sludge thickener discharge. The sludge thickener sample is a grab sample taken by the wastewater treatment plant (WWTP) operator by dropping a bottle into the thickener between the overflow weir and the thickener sidewall. The clarifier sample and thickener sample are flow-proportioned at the Quality Assurance/Quality Control (QA/QC) laboratory. The grab sample location is not representative of the actual thickener discharge. Jay Rankin stated there is no feasible sample location where the thickener discharges to outfall 002. Outfall 002 compliance monitoring is also inaccurate because of the flow measuring deficiencies.

CLEAN WATER ACT - SPILL PREVENTION CONTROL AND COUNTERMEASURES

The following areas of concern of the SPCC requirements were identified during the NEIC investigation.

- Shell's stormwater detention area has the potential to overflow and impact Grassy Lake. A release occurred on April 25, 1993 during a large storm event which washed oil and water from the detention area. The oil reached Grassy Lake through Shell's NPDES outfall 003. The stormwater detention area appears to be filling with sediment, reducing its capacity. According to Jay Rankin, Senior Engineer, the detention area was probably constructed in the 1940s and has not been dredged to his knowledge.

- Shell's SPCC Plan is general, discussing major SPCC components without providing much detail. The plan does not include a tank list or any indication of the refinery's type, location, or capacity of oil storage. The plan does not indicate the largest magnitude of spill possible or a discussion of spill history at the refinery. The plan does not discuss spills associated with incoming crude delivery or distribution of oil products. Although there is discussion regarding response personnel and communication, no person is designated in the plan with overall responsibility for the SPCC program. Also, no emergency response contacts are listed in the plan.

- If the proposed SPCC regulations are adopted, Shell would be required to update their SPCC Plan. In response to several notable oil spills in the U.S., revisions to the SPCC regulations were proposed (Federal Register, Vol. 56, No. 204, October 22, 1991) to strengthen and clarify current regulatory provisions. The proposed regulations intend to provide clarification by changing current "guidelines" to requirements, particularly those provisions currently under 40 CFR § 112.7 - Guidelines for the preparation and implementation of an SPCC plan.

- If proposed SPCC regulations are adopted, Shell may be required to improve their earthen dikes to reduce the permeability. One proposal requires diked areas for bulk containers to be sufficiently

impervious to contain spilled oil for at least 72 hours. While some dike walls are asphalt coated, the floors are not and may not be impervious to oil for 72 hours. The current regulations state that diked areas should be "sufficiently impervious" to contain spilled oil.

SAFE DRINKING WATER ACT - UNDERGROUND INJECTION CONTROL

The following concern regarding the UIC requirements was identified during the NEIC investigation.

- Shell has not notified IEPA and/or the city of Roxana that the facility does not have any Class V injection wells.

RESOURCE CONSERVATION AND RECOVERY ACT - HAZARDOUS WASTE MANAGEMENT

The following areas of noncompliance and area of concern of the hazardous waste management requirements, including Title 35 of the Illinois Administrative Code (IAC), were identified during the NEIC investigation.

Areas of Noncompliance

35 IAC § 722.134(a)(3) [40 CFR § 262.34(a)(3)]	The following containers were not labeled or marked with the words "Hazardous Waste."

- One hundred and seventy flow bins of spent catalyst
- Two bins of bar screen debris

RCRA Permit 1191150002 J.3	Drums stored in the CATCO building were not properly marked. • Two drums were not marked with the EPA hazardous waste number • Sixteen drums were not marked with the waste group number • Thirty-two drums were not marked with a container identification number
35 IAC § 722.134(a)(2) [40 CFR § 262.34(a)(2)]	Two bins of bar screen debris were not marked with the date upon which each period of accumulation begins.
35 IAC § 722.120(a) [40 CFR § 262.20(a)]	Eight drums of hazardous waste were not manifested from the West Property to the Main Property. The hazardous waste is transported along a public road from the West Property to the Main Property.
35 IAC § 722.112(a) [40 CFR § 262.12(a)]	Hazardous waste has been offered for transportation from the West Property without Shell receiving an EPA Identification Number.
35 IAC § 728.107(a)(1) [40 CFR § 268.7(a)(1)]	Ninety-one primary solids and slop oil emulsion LDR notifications were incomplete or incorrect. Missing or incorrect information included: treatment standards and EPA hazardous waste numbers.
35 IAC § 728.107(a)(1) [40 CFR § 268.7(a)(1)]	Eighty-eight LDR notifications were not sent to the treatment or storage facility with the waste shipment.

Area of Concern

- Process wastewater discharged to the sewer system contains benzene above the toxicity characteristic regulatory level for a characteristic hazardous waste, and has leaked into the surrounding soil. NEIC

collected and analyzed two samples (November 3 and 4, 1993) from the master box. The master box is a sampling point, on the Main Property, where all process waste streams combine. Sample analytical results show that wastewater sampled from the master box is a RCRA characteristic hazardous waste for the toxicity characteristic of benzene. The sample results range from 2.7 ppm to 3.7 ppm. Various portions of the sewer have been replaced in the past due to leaks in the lines. Because there have been leaks in the sewer lines in the past, hazardous waste may have been disposed.

RESOURCE CONSERVATION AND RECOVERY ACT - UNDERGROUND STORAGE TANKS

Based on discussions with Shell personnel and review of available documents, Shell has no underground storage tanks in service. Shell removed from service 10 USTs in November 1989, and 1 in February 1991. No other USTs were identified during the NEIC on-site inspection.

EMERGENCY PLANNING AND COMMUNITY RIGHT-TO-KNOW ACT

The following areas of noncompliance and areas of concern of the Emergency Planning and Community Right-to-Know Act requirements were identified during the NEIC investigation.

Areas of Noncompliance

40 CFR § 302.6(a)	Shell's notifications to National Response Center (NRC) for 12 reportable releases were not made immediately following the release.

40 CFR 355.40(b)(1)	The state emergency response commission and the local emergency planning committee were not immediately notified of 12 reportable releases.
40 CFR § 372.30(a)	Shell failed to report approximately 15,000 pounds of cobalt transferred off-site for disposal or recycling during 1990.
	Shell failed to report approximately 68,000 pounds of molybdenum trioxide transferred off-site for disposal or recycling during 1990.
	Shell failed to report sulfuric acid transferred off-site in 1991 and 1992. Shell personnel indicated that millions of pounds of sulfuric acid are annually transferred off-site for recycling.

Areas of Concern

- Shell does not report all releases above the reportable quantity. The 1,000 ppm SO_2 emission limit for the sulfur recovery unit (SRU) was exceeded on 28 occasions from February 1991 through October 1993. During the excess emissions, the quantity of SO_2 released ranged from 25 pounds to 1,576 long tons. The operating permit for the SRU allows excess emissions provided that the Illinois Environmental Protection Agency is notified immediately. Shell considers these incidents permitted releases and does not report them to the state and local emergency committees.

- Fugitive benzene emissions from the cooling towers were calculated to be over 94,000 pounds. Remediation groundwater extracted for use in the refinery cooling towers is contaminated with benzene. Several wells are used to extract the contaminated groundwater with benzene concentrations ranging from 0 to 52 ppm. Based on large flows (approximately 3,400 gpm combined flow) the amount of benzene contained in the extracted water is 94,800 pounds. All the benzene is assumed to be released to the atmosphere.

TOXIC SUBSTANCES CONTROL ACT

The following area of concern regarding the PCB requirements was identified during the NEIC investigation.

- Shell has not tested the heat transfer systems at the alkylation/benzene extraction unit for PCBs.

LABORATORY EVALUATION

The following areas of noncompliance and area of concern of the laboratory operating requirements associated with NPDES permit requirements were identified.

Areas of Noncompliance

40 CFR § 136.3	Inappropriate containers or chemical preservatives were being used for samples analyzed to determine compliance with the NPDES permitted levels for phenols, sulfides, and hexavalent chromium.
40 CFR § 136.3	Samples collected for analysis by NPDES permitted tests, including samples of phenols, sulfides, hexavalent chromium, total chromium, oil and grease, BOD_5, chemical oxygen demand, ammonia, and total cyanide were not being stored at the required temperature of 4 °C.

40 CFR § 136.3	pH determinations are not performed immediately after taking the sample.
Standard Method 5210, as referenced in 40 CFR § 136.3	The BOD_5 incubator does not maintain the temperature at 20 °C ± 1 °C.
Standard Method 4500-NH_3 G, as referenced in 40 CFR § 136.3	The ammonia determination is not properly conducted. The lab does not use *Standard Method* 4500-NH_3 B prior to measurement with *Standard Method* 4500-NH_3 G.
40 CFR § 136, Appendix B and 40 CFR § 136, Appendix C, Section 12	Method 200.7 for the determination of total chromium was not followed; an insufficient number of calibration blanks were performed and the procedure for determination of the method limit of detection (LOD) was not performed.

Area of Concern

- The Shell laboratory QA/QC program for analyzing NPDES permitted parameters is inadequate in the following areas:

  - Individual sample containers collected by the treatment plant operator(s) lacked unique identification.
  - Sample chain-of-custody procedures were incompletely followed.
  - Written SOPs for the cleaning of laboratory glassware were not followed.
  - A record of the preparation of standards is not kept.
  - Only a single standard is prepared, diluted as needed, and then used to calibrate, check calibration, and spike samples.
  - Daily calibration checks are not performed for most tests.
  - Instrument calibration curves were not produced on a sufficiently regular basis.

  - Analytical method blanks are not being performed.
  - No records exist for the determination of the LOD for the tests being performed.
  - Execution of the concept of batch QC is inadequate
  - No procedure is available for denoting suspect test results
  - Potential problems exist with shared usage of equipment

GLOSSARY

GLOSSARY

ACM: asbestos containing materials
BEST: Building Environmental and Safety Traditions
BOD_5: biochemical oxygen demand
BPD: Barrels per day
BTEX: benzene, toluene, ethylbenzene, and xylenes
CAA: Clean Air Act
CAU: Cracked Absorption Unit
CCU: Catalytic Cracking Unit
CDU: catalytic dewaxing unit
CEM: continuous emission monitor
CERCLA: Comprehensive Environmental Response and Liability Act
CFH: Catalytic Feed Hydrotreater
CFR: Code of Federal Regulations
COD: chemical oxygen demand
CPI: corrugated plate interceptor
CR: Catalytic Reformer
CWA: Clean Water Act
DAF: dissolved air flotation
DAU: deasphalting unit
DEA: diethanolamine
DHT: Distillate Hydrotreater
DMR: discharge monitoring report
DU: Distilling Unit
EHS: Extremely Hazardous Substance
EPCRA: Emergency Planning and Right-to Know Act
ESDA: Emergency Services and Disaster Agency
ESP: Electrostatic Precipitator
FRP: fiberglass reinforced plastic
gr/dscf: grains per dry standard cubic foot
gpm: gallon per minute
HCU: Hydrocracker Unit
HDU: Hydrodesulfurization Unit
H_2S: hydrogen sulfide
HSWA: Hazardous and Solid Waste Amendments
IAC: Illinois Administrative Code
IEPA: Illinois Environmental Protection Agency
KHT: Kerosene Hydrotreater
KO: Knock-out pot
LDAR: Leak Detection and Repair
LDR: Land Disposal Restriction
LHT: Lubricants Hydrotreater
LOD: limit of detection
LTD: long tons per day
MBPD: million barrels per day
MDEA: methyldiethanolamine
MDO: maintenance dropout tank
MEP: major effluent treatment project
mgd: million gallons per day
Mg/yr: Mega grams per year
MMBtu: million British thermal units
mL: milliliter
MOV: motorized valve
MTBE: Methyl tert butyl ether
MSDS: material safety data sheet
NEIC: National Enforcement Investigations Center
NESHAP: National Emission Standards for Hazardous Air Pollutant
NH_3: ammonia
NMP: N-methyl-2-pyrolidinone
NPDES: National Pollutant Discharge Elimination System
NRC: National Response Center
NSPS: New Source Performance Standard
OPA: Oil Pollution Act
OSRP: Oil Spill Response Plan
PCB: polychlorinated biphenyl
PID: piping and instrumentation drawing
PPE: personnel protective equipment
ppm: parts per million
PRV: pressure relief valve
PSIG: Pounds per square inch gauge
QA/QC: Quality Assurance/Quality Control
RA: Raffinate Absorber
RAU: Rectified Absorber Unit
RCRA: Resource Conservation and Recovery Act
RDC: rotating disk contactor

RFG: refinery fuel gas
RFP: refinery fuel pitch
SARA: Superfund Amendments and Authorization Act
SCOT: Shell Claus off-gas treating unit
SGP: Sour gas plant
SO_2: sulfur dioxide
SOP: standard operating procedure
SDWA: Safe Drinking Water Act
SMR: steam methane reformer
SOG: source operating group
SPCC: Spill Prevention Control and Countermeasures
SRU: sulfur recovery unit
SWS: sour water stripper
TAB: total annual benzene
TCLP: Toxicity Characteristic Leaching Procedure
TDS: total dissolved solids
TLV: threshold limit value
TOC: total organic carbon
TSCA: Toxic Substance Control Act
TSDF: treatment, storage, and disposal facility
TSS: total suspended solids
UIC: Underground Injection Control
UST: underground storage tank
VBU: Visbreaker Unit
VFU: Vacuum Flashing Unit
VHAP: Volatile hazardous air pollutants
VOC: volatile organic compound
WRR: Wood River Refinery
WWTP: wastewater treatment plant

TECHNICAL REPORT

PROCESS DESCRIPTION/WASTE GENERATION

MULTI-MEDIA COMPLIANCE INVESTIGATION

Shell Oil Company
Wood River Manufacturing Complex
Roxana, Illinois

Facility Address

Shell Oil Company
Wood River Manufacturing Complex
Highway 111
Roxana, Illinois 62084
(618) 255-2478

Investigation Dates

October 25 through November 5, 1993

Lead Investigator

Linda TeKrony, Environmental Engineer
NEIC

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Prevention

REFINERY PROCESS DESCRIPTION/WASTE GENERATION

GENERAL

This section provides a brief summary of the refinery process operations and identifies waste streams generated. Information presented in this section consists of company-provided process information and oral descriptions by company representatives.

The refinery processes up to 250,000 barrels per day (bpd) of crude oil and can process high sulfur (greater than 2%) crudes. Crude arrives by pipeline, from sources within the United States and overseas. Figure 1 is a site map of the refinery.

The refinery processes oil through a series of distillation, cracking, reforming, hydrotreating, and blending operations. A simplified process flow diagram for the major refinery operations is presented in Figure 2. Distillation columns separate hydrocarbon groups (fractions) by using differences in boiling points. Cracking involves splitting long-chained hydrocarbons into shorter ones. Reforming converts straight-chain hydrocarbons into branched hydrocarbons or cyclic aromatics such as benzene, toluene, and xylene. Hydrotreating operations involve sulfur removal, nitrogen removal, and product purification. Blending operations produce many products by mixing various intermediate hydrocarbons. Major process units and their capacities are listed in Table 1.

During the processing of crude oil, many solid wastes, air emissions, and wastewater streams are generated. The major waste streams for each of the processing units are identified in Table 2 and discussed in more detail in the appropriate media report.

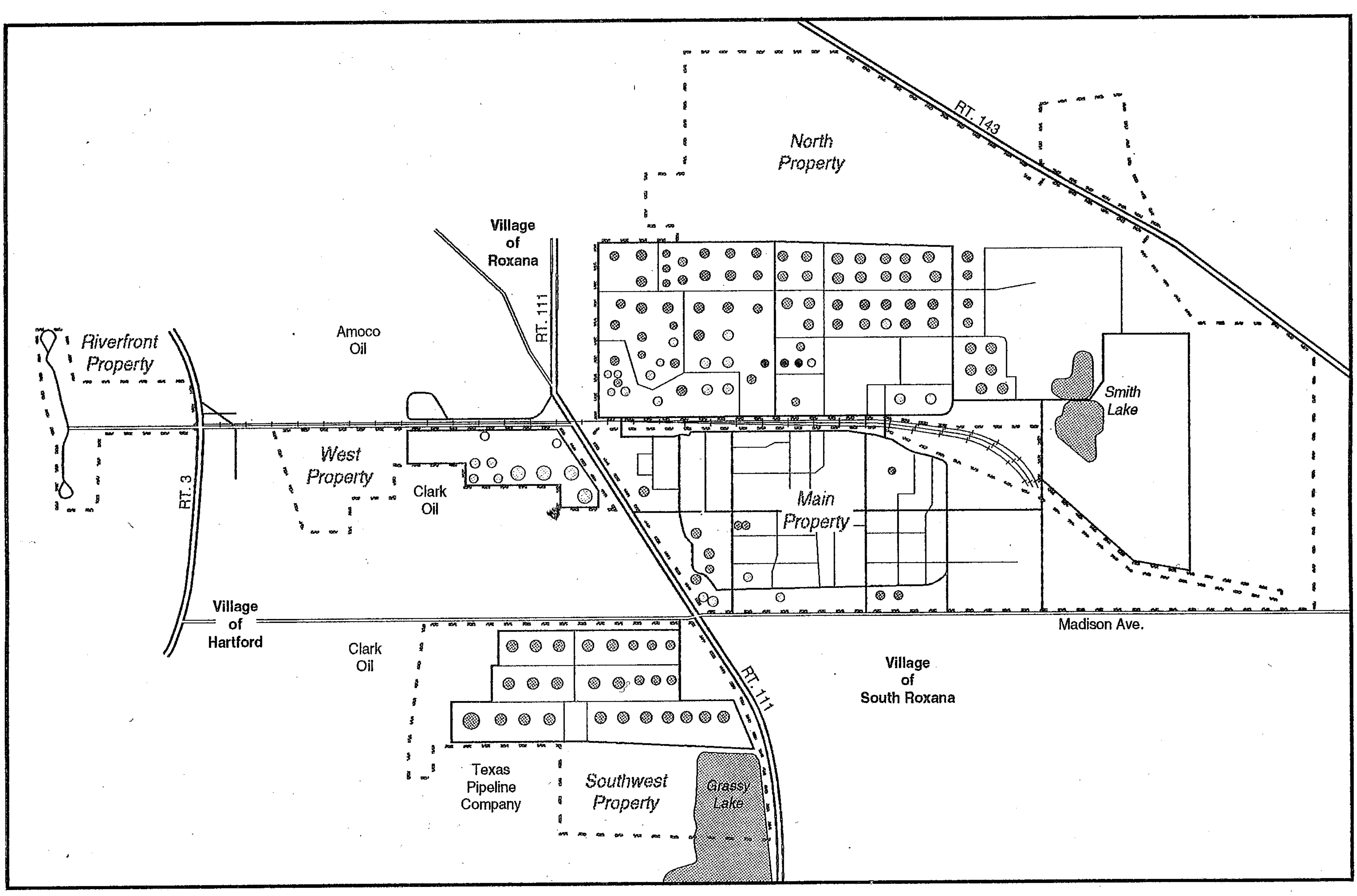

Figure 1
SITE MAP
Shell Oil Company
Wood River Manufacturing Complex
Roxana. Illinois

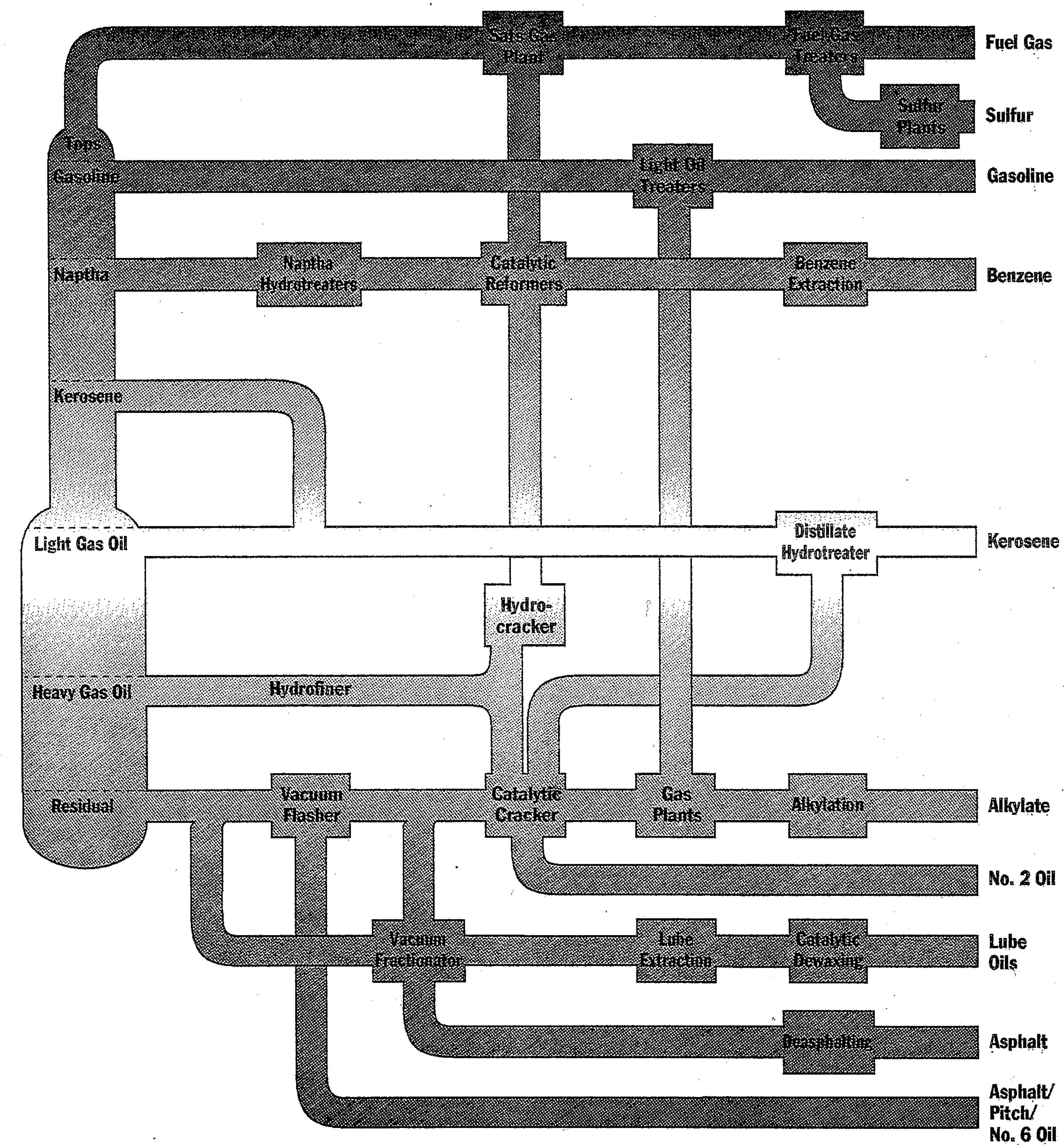

Figure 2
PROCESS FLOW DIAGRAM
Shell Oil Company
Roxana, Illinois

Table 1

MAJOR PROCESS UNITS AND CAPACITIES
Shell Oil Company
Roxana, Illinois

Unit	Capacity (MBPD)[1]	Unit	Capacity (MBPD)
Distilling/Gas Department			
Distilling Units	273	Vacuum Flasher Units	98.5
Visbreaking	16.6	Naphtha Hydrotreater	61
Cracking/Alkylation Department			
Catalytic Cracking Units	80	Catalytic Feed Hydrotreater	22.5
Alkylation	20	---	---
Hydroprocessing Department			
Hydrocracking	19	Catalytic Reforming Units	84
Kerosene Hydrotreating	23	Distillate Hydrotreating	48.5
Lubricants Department			
Hydrotreater	10	Deasphalting Unit	2.2

[1] *1,000 barrels per day*

Table 2

MAJOR WASTE STREAMS/SOURCES FOR REFINERY OPERATIONS
Shell Oil Company
Roxana, Illinois

Process/Areas	Solid Waste	Air Sources[1]	Wastewater Source/Stream[2]
Distilling/Gas Department			
Distilling Units		Heaters, vents	Sour water
Vacuum Flasher Units		Heaters	Sour water
RAU & CAU Gas Plants			Sour water
Light Oil Treaters		Heater, vents	Sour water
Sour Water Stripper System	Filters		Stripped sour water
Cracking/Alkylation Department			
Alkylation Unit	Sulfuric acid	Heaters, vents	Spent caustic
Benzene Extraction Unit	Sulfolane bearing water Filters Clay contactors	Heaters	
Catalytic Cracking Units	Reactor catalyst	CO boiler, heaters, ESP stacks	Sour water
Catalytic Feed Hydrotreater	Reactor catalyst	Heater	Sour water
Hydroprocessing Department			
Catalytic Reformers	Reactor catalyst	Heaters, vents	Sour water Spent caustic Oil/water separators

[1] *Fugitive VOCs are released from all process areas.*
[2] *Numerous noncontact cooling waste sources are discharged from the process areas.*

Table 2 (continued)

Process/Areas	Solid Waste	Air Sources[1]	Wastewater Source/Stream[2]
Hydroprocessing Department			
Distillate Hydrotreaters	Reactor catalyst	Heaters	
Hydrocracker	1st stage catalyst 2nd stage catalyst	Heaters, vents	Sour water
Hydrodesulfurization Units	Reactor catalyst	Heater	
Kerosene Hydrotreater	Reactor catalyst	Heater	
Saturates Gas Plant	Diethanolamine	Heater	Water/caustic flash pots
Steam Methane Reformer	High temperature shift catalyst Low temperature shift catalyst Reformer catalyst Methanator catalyst Zinc oxide		Water from knock out pots
Lubricants Department			
Catalytic Dewaxing Unit	Dewax catalyst Hydrotreating catalyst Drying material	Heater	Sour water
Hydrotreater	Reactor catalyst	Heater, vents	
Vacuum Fractionator Column			Oily water
Lube Extraction Unit		Heaters	
Deasphalting Unit		Heaters	Sour water

[1] *Fugitive VOCs are released from all process areas.*
[2] *Numerous noncontact cooling waste sources are discharged from the process areas.*

Table 2 (continued)

Process/Areas	Solid Waste	Air Sources[1]	Wastewater Source/Stream[2]
Miscellaneous			
Sulfur Plant	Claus 1st stage catalyst Claus 2nd stage catalyst SCOT catalyst Charcoal filter	Claus train Tail gas vents Incinerator Emergency scrubber Sulfur loading racks	Sour water
Miscellaneous	Leaded tank bottoms Heat exchanger cleaning sludge Primary solids Filter cloths from primary solids presses Used personnel protective equipment Bar screen debris Lead contaminated paint waste Lime sludge filter cake	Boilers Flares Storage tanks Barge loading terminal Truck loading terminal Emergency generators Cooling towers	Cold lime sludge dewatering Boiler feed water treatment

[1] Fugitive VOCs are released from all process areas.
[2] Numerous noncontact cooling waste sources are discharged from the process areas.

PROCESS DESCRIPTION

Operating rates for each process can be varied to account for different crude feed mixes and seasonal product demand. Shell has divided most of the processing portion of the refinery into four departments: Distilling/Gas, Cracking/Alkylation, Hydroprocessing, and Lubricants. Some processes, such as Sulfur Recovery, are discussed in a miscellaneous section.

Distilling/Gas Department

Process units operated in this department include two distilling units, three vacuum flashers, two gas plants, light oil treaters, and a sour water stripper system.

Distilling Units

Shell operates two multi-stage distillation crude units. Crude is treated in a two-stage desalter to remove salt and other impurities prior to entering the distilling units. Distilling unit No. 1 is comprised of two columns, and distilling unit No. 2 is comprised of three columns.

Distilling Unit No. 1

An electrostatic desalting system treats the distillation feed crude prior to entering the columns. Salt is removed from the crude in the aqueous phase and is discharged to the wastewater treatment plant. The desalting wastewater stream represents approximately 5% of the crude entering the columns.

Heat exchangers heat the crude prior to entering the primary column. Distillation uses differences in hydrocarbon boiling points to separate the crude into fractions consisting of closely grouped boiling point hydrocarbons. Column design and product specification are used to determine the feed injection point, overhead recycle rate, and collection point for each fraction.

Several hydrocarbon fractions (or streams) are removed from the primary column. In general the lighter hydrocarbons are removed from the top of the column and the heavier hydrocarbons are removed from the lower portion of the column. The overhead or low boiling point stream is mainly naphtha fractions. The high boiling point hydrocarbons (bottoms) from the primary column are used as the feed to the secondary column.

Primary column overheads are processed in a stabilization section that consists of a depropanizer column, a debutanizer column, and a deisohexanizer column. Four products are produced from the stabilization section: Fuel gas (vapor tops from the debutanizer column), saturates gas plant feed (vapor and liquid tops from the depropanizer column), straight run gasoline (liquid tops from the deisohexanizer column), and light naphtha (liquid bottoms from the deisohexanizer column).

Primary column bottoms are sent to the secondary column for further separation. Products from the secondary column include: naphtha, kerosene, light gas oil, heavy gas oil, extra-extra heavy gas oil, and a residual. The naphtha is further processed in distilling unit No. 2; kerosene and light gas oil are hydrotreated; heavy gas oil and extra-extra heavy gas oil are used as feed to the catalytic cracker; and the residual is processed in a vacuum flasher to produce asphalt.

Distilling Unit No. 2

Distilling unit No. 2 operates similarly to distilling unit No. 1, except that there are three distilling columns: mixed crude column, lube crude column, and the upper column. This unit is used to process lube and asphalt crudes.

Crude is fed to the mixed crude column after desalting and heating. The mixed crude column produces heavy gas oil and extra heavy gas oil (feed to the catalytic cracker) and a residue (feed to a vacuum flasher).

Crude is fed to the lube crude column after the desalters scrub the crude of salts and solids and the crude has been heated. The lube crude column produces heavy gas oil (feed to catalytic cracking) and a residual (feed to vacuum fractionator column).

The tops from both the mixed crude column and the lube crude column are combined to feed the upper column. The upper column further separates the feed into fractions. Fractions produced by the upper column include: straight run light gas oil, kerosene, and heavy naphtha. These fractions will receive further treatment at other units before producing the finished products of furnace oil or diesel fuel, jet fuel, and a gasoline blending component called reformate.

<u>Vacuum Flasher Units</u>

The vacuum flasher units are designed to process straight run residuals from the distilling units and produce several products including: extra heavy flashed distillate, heavy flashed distillate, light flashed distillate, and distillate bottoms. The feed into the system is heated in two furnaces prior to entering the vacuum flasher sphere. Liquid and vapor oil flow in a circular direction around the sphere to separate the liquid and vapor components. The vapor is further processed and routed to the catalytic crackers. The liquid phase is called pitch which is used in process heaters and boilers as a fuel, or is routed to asphalt storage.

Rectified Absorption Unit and Cracked Absorption Unit

Two gas plants are used to separate the light ends from several streams generated at the catalytic cracking units. Propanes and butanes are removed from the feed in two separate columns. Bottoms from the debutanizer column are further processed in the light oil treaters. Tops from the depropanizer and debutanizer columns are routed to the alkylation unit.

Light Oil Treaters

Light oil treaters remove or convert mercaptans and residual traces of hydrogen sulfide (H_2S) to disulfides in finished gasoline. Caustic removes certain mercaptans from the gasoline. Any remaining mercaptans are oxidized to disulfides by mixing the gasoline with air and caustic. Conversion of the mercaptans to disulfides does not reduce the amount of the sulfur that remains in the gasoline. The final processing step of the light oil treaters is removal of the entrained caustic from the treated gasoline before it is sent for blending.

Sour Water Stripper System

Sulfides and ammonia (NH_3) are removed from the refinery's sour water prior to disposal. Stripped sour water is disposed of in the process sewer. The

feed to the sour water stripper consists of sour water from the hydrocracker, saturates gas plant, catalytic crackers, catalytic feed hydrotreater, and vacuum flashers. The sour water is steam stripped in a packed column. The overhead stream, containing high amounts of NH_3 and sulfides, is condensed and routed to the sulfur plant sour water stripper. The bottoms from the stripper are routed to the distilling desalter or the process sewer.

Cracking/Alkylation Department

Process units operated in the department include: catalytic feed hydrotreater, catalytic cracking units, alkylation unit, and the benzene extraction unit.

Catalytic Feed Hydrotreater

The purpose of this unit is to remove sulfur, nitrogen containing compounds, and trace metals such as nickel and vanadium from gas oil. The "clean" gas oil is used as feed to the catalytic crackers. Impurities in the gas oil are extremely corrosive and may deactivate (poison) the catalyst in the catalytic crackers. This process is essentially a pretreatment step for the catalytic crackers.

Gas oil and excess hydrogen are added to the reactor vessels under high pressure and temperature. Catalyst fixed in the reactors promotes the removal of the sulfur and produces an H_2S gas, which is removed in the light ends fraction. Nitrogen impurities in the feed stream are removed as NH_3 in a similar manner. The metals are plated out on the active sites of the catalyst surface.

Catalytic Cracking Units

A catalytic cracking unit (CCU) is used to split long-chain hydrocarbons into shorter hydrocarbons. A catalyst, alumina/silicate, promotes this chemical reaction. The CCU consists of two main vessels: The reactor and the regenerator. The catalyst is continuously circulated through the reactor and regenerator.

Hydrocarbon feed to the CCU is preheated and introduced to the catalyst at the bottom of the reactor. The cracking of the feed is accomplished within a few seconds as the material moves up through the reactor. The catalyst and the hydrocarbon products are separated at the top of the reactor. The hydrocarbon products are cooled and distributed to other parts of the refinery for further processing, and the catalyst flows to the regenerator.

Coke is deposited on the catalyst during the cracking process and hinders catalyst efficiency; therefore, the catalyst must be regenerated. Catalyst regeneration involves the use of air to fluidize the catalyst and burn off the coke. Clean catalyst is reintroduced into the reactor to start the process. A portion of the spent catalyst is removed from the regenerators on a routine schedule and a corresponding quantity of fresh catalyst is added.

Alkylation

The purpose of this unit is to convert butenes and isobutane, produced in other parts of the refinery, into a useable blending stock for gasoline. Sulfuric acid is used as a catalyst to promote the reaction and is continuously pumped through the alkylation reactors. The reaction of the hydrocarbons is relatively slow. The product stream from the alkylation reactor is washed with

caustic to remove any remaining acid. Spent sulfuric acid removed from the system is sent off-site for regeneration.

Benzene Extraction Unit

The benzene extraction unit selectively recovers benzene from light reformate. Other products from this unit include toluene concentrate and washed raffinate, which are used as finished gasoline blending components.

Two distillation columns are operated in semi-parallel operation to concentrate the benzene. The columns are operated so that the majority of benzene goes to the overhead and toluene is taken from the second column bottoms, and used as a gasoline blending component. The tops from the two columns are combined and fed to one of two extractor rotating disk contactors (RDC).

Sulfolane is used in the RDC-1 to preferentially extract the benzene from the column tops. Tops from RDC-1 are routed to RDC-2. The bottoms, consisting of sulfolane and benzene, are routed to the paraffin stripper column.

RDC-2 removes any sulfolane that has dissolved into the raffinate. Water is used to remove the sulfolane. The water and sulfolane leave the bottom of the extractor and are processed in a water still. The washed raffinate is stored for use in finished gasoline blending.

The paraffin stripper column removes paraffins from the sulfolane/benzene mixture. Bottoms of the paraffin stripper are fed to a solvent recovery column, where the benzene is separated from the sulfolane. Both stripping steam and vacuum operation are employed to aid this separation. The overhead vapors from the solvent recovery column are condensed and separated in an accumulator into a benzene phase and a water phase. The water phase is run through a water still and reused as wash water in the RDC-2.

The benzene phase is further processed using clay contactors and a finishing column. The purpose of the clay contactors is to polymerize olefins in the benzene which will be removed in the finishing column. Water is removed from the top of the finishing column, benzene is removed as a side stream, and the bottoms are routed back to the distillation column at the beginning of the benzene extraction unit.

Hydroprocessing Department

Process units operated in the department include: hydrodesulfurization units, catalytic reformers, distillate and kerosene hydrotreaters, hydrocracker, saturates gas plant, and steam methane reformer.

Hydrodesulfurization Units

The purpose of the hydrodesulfurization unit is to remove sulfur and nitrogen from the light naphtha stream produced from the deisohexanizer column. Sulfur and nitrogen must be removed because they will deactivate the catalysts in the catalytic reformers, the next processing unit. Sulfur and nitrogen are removed by conversion to H_2S and NH_3, which are subsequently removed.

Catalytic Reformers

Three catalytic reformers are used to increase the octane number of the feedstock. This is accomplished by converting the straight hydrocarbons (naphtha) into branched, multi-bond, or cyclic (aromatic) hydrocarbons. Metal catalysts, located within the reactors, promote this conversion. Hydrogen produced in this process is used in other refinery processes.

Catalytic reformers No. 1 and 3 each consist of five reactors with one reactor being regenerated at any one time. Regeneration includes burning coke absorbed on the catalyst, neutralizing the acid gas produced during coke burning, redispersing the catalyst metal, and reducing the metal to its metallic form, which is the active state for catalytic reforming.

Catalytic reformer No. 2 is a semi-regenerative unit. The reactor area is used as the regeneration area, and the process is taken out of service while the catalyst is being regenerated.

Distillate Hydrotreaters

The purpose of the distillate hydrotreaters is to prepare a finished kerosene and furnace oil/diesel product meeting sulfur and particulate specifications. In 1993 the distillate hydrotreaters were modified to produce furnace oil/diesel product meeting the low-sulfur requirements, as outlined in the 1990 Clean Air Act. The distillate hydrotreater consists of three catalyst filled reactors: the first reactor largely serves as a scale and fouling catcher, the second reactor reduces the product sulfur level to approximately 0.30% by weight, and the third reactor further reduces the sulfur level to approximately 0.044%.

Kerosene Hydrotreater

The kerosene hydrotreater processes distillate and heavy naphtha in two main sections. In the reaction section, kerosene or heavy naphtha and hydrogen rich gas are combined, heated, and passed over a catalyst. The hot reactor products are subsequently cooled and flashed into gas and liquid phases. In the stabilizer section, H_2S is removed from the cooled reactor liquid in order to produce a liquid product suitable for "Jet A" product or catalytic reformer feed. The vent gases flow to the Distillate Hydrotreater.

Hydrocracker

The hydrocracker converts a mixture of straight run and catalytically cracked gas oils into gasoline and lighter products. Hydrogen is used in the process to: remove nitrogen and sulfur containing compounds, hydrogenate aromatic compounds, and saturate light olefins formed during the cracking reaction. The hydrocracker consists of four major sections.

- Hydrogen make-up section that absorbs light hydrocarbons from low purity hydrogen streams.
- First stage hydrotreating section removes nitrogen compounds.
- Second stage hydrotreating section converts first stage product to gasoline and lighter components.
- Product purification and fractionation section

Overheads from the fractionator are routed to the saturates gas plant. Heavy naphtha is fed to one of the catalytic reformers.

Saturates Gas Plant

The saturates gas plant recovers and separates light and heavy hydrocarbons present in the refinery gas. This recovery and separation process produces: a refinery gas that may be used as fuel, propane, mixed butanes, a hydrogen sulfide-rich amine solution, gasoline blending stock, and catalytic reformer feedstock. The gas plant consists of a rectified absorber column, sponge column, debutanizer column, depropanizer column, and treating systems. The various columns are used to separate the fractions of refinery gas and produce usable products including: propane, gasoline blending stock, and catalytic reformer feedstock.

The treating systems remove H_2S from the feed to the steam methane reformer and the liquid propane and butanes from the debutanizer column. H_2S removal is accomplished by contacting the gas and liquid streams with diethanolamine (DEA). The "fat" DEA is used as a scrubbing fuel before being sent to the sulfur plant for regeneration and sulfur recovery.

Steam Methane Reformer

The steam methane reformer produces hydrogen. Various refinery off-gas streams containing hydrogen and light hydrocarbons are collected and treated for sulfur removal. Treated feed gas and steam are fed to the furnace, the main processing unit. Hydrogen is formed in the catalyst-filled tubes of the reformer furnace, along with carbon monoxide and carbon dioxide. Carbon monoxide is converted to carbon dioxide in catalyst filled shift converters. The carbon dioxide, and trace amounts of carbon monoxide are converted back to methane, which remains in the hydrogen gas stream.

Lubricants Department

Process units operated in this department include a vacuum fractionator column, lube extraction unit, hydrotreater, catalytic dewaxing unit, and deasphalting unit.

Vacuum Fractionator Column

Feed to the vacuum fractionator column is the straight run residue from distilling unit No. 2. Vacuum fractionation separates the lube feedstock into a number of different boiling range components. This fractionation is carried out under vacuum because of the high boiling range in the lube feedstock.

Lube Extraction Unit

The purpose of the lube extraction unit is to remove aromatic compounds from the waxy distillates or deasphalted short residue previously processed in the vacuum flasher column. The feed is separated into two liquid phases using a liquid-liquid extraction with N-methyl-2-pyrrolidinone (NMP) as the solvent. Aromatics migrate to the NMP phase while the paraffinic compounds remain in the oil phase. NMP is recovered from the raffinate using a flash vessel and a steam stripper. The product raffinate is routed to the hydrotreater and eventually to the catalytic dewaxing unit for further processing.

Hydrotreater

Lube hydrotreating supplements the extraction process by improving several characteristics of the lube oil. Extraction improves the color, viscosity index, and oxidation stability by physical separation of undesirable compounds. Hydrotreating alters these compounds through chemical reaction with hydrogen and a catalyst. The lube hydrotreater saturates aromatics and removes sulfur and nitrogen containing compounds.

Catalytic Dewaxing Unit

Lubricating oils (lube oils) are processed through the catalytic dewaxing unit. Hydrogen is purified by removing potential catalyst poisons such as carbon monoxide, carbon dioxide, water, NH_3, and H_2S. The lube oils are combined with the hydrogen and fed to a catalyst filled reactor where the wax molecules are cracked to lighter material. The lube oils and cracked material are then processed to remove the light gases and naphtha by-products that are formed during the dewaxing process.

Deasphalting Unit

The purpose of the solvent deasphalting unit is to remove asphaltic material from the bottoms of the vacuum fractionator (short residue) prior to further processing in the lube extraction unit. Propane is contacted with the short residue to extract the asphaltic material. The deasphalted oil is processed further at the lube extraction unit. The asphalt is used in finished asphalt or blended into No. 6 fuel oil. The propane is recovered for reuse.

Miscellaneous

Sulfur Plant

The sulfur plant consists of the following units: DEA system, sour water stripper (SWS), three Claus trains, and three Claus off-gas treating (SCOT) units.

The DEA system removes the H_2S and NH_3 (acid gas) from the "fat" DEA that is received from Shell and two adjacent facilities. Three DEA strippers operate to remove the acid gas from the DEA. The stripper bottoms are "lean" DEA which is returned to the various facilities. The stripper tops are condensed and sent to the SWS.

In the SWS column, NH_3 and H_2S are steam stripped from the sour water by direct steam injection. The vapor tops are routed to the ammonia combustors prior to the Claus trains. The ammonia combustor converts NH_3 to nitrogen gas.

The Claus trains convert H_2S to elemental sulfur in the presence of a catalyst and sulfur dioxide (SO_2). The sulfur gases pass through the first catalyst bed where most of the H_2S and SO_2 are converted to sulfur. A second catalyst bed is used to convert any remaining H_2S and SO_2 to sulfur.

Associated with each Claus train is a SCOT unit used to convert all the leftover sulfur compounds to H_2S, which is recycled back to the Claus trains. A catalyst is used to promote the conversion of the sulfur compounds to H_2S. Following the conversion, an adsorption process is used to separate the H_2S from the other gases. Methyldiethanolamine (MDEA) contacts the gases and

selectively absorbs the H_2S. A stripper is used to remove the H_2S from the MDEA. The stripped H_2S is recycled back to the Claus trains and the MDEA is reused in the absorption process.

POLLUTION PREVENTION

MULTI-MEDIA COMPLIANCE INVESTIGATION

Shell Oil Company
Wood River Manufacturing Complex
Roxana, Illinois

Facility Address

Shell Oil Company
Wood River Manufacturing Complex
Highway 111
Roxana, Illinois 62084
(618) 255-2478

Investigation Dates

October 25 through November 9, 1993

Lead Investigator

Linda TeKrony, Environmental Engineer
NEIC

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MEDIA REPORT

At the request of EPA Region 5, NEIC conducted a multi-media compliance investigation of the Shell Oil Company - Wood River Manufacturing Complex (Shell) located in Roxana, Illinois. This report, one of a series for the multi-media compliance investigation, discusses pollution prevention issues at Shell.

REGULATORY SUMMARY

The Pollution Prevention Act of 1990 established the promotion of pollution prevention as a national policy of the United States. EPA has established a pollution prevention strategy, and set general guidelines and objectives. The Hazardous and Solid Waste Amendments of 1984 (HSWA) mandated minimization of hazardous waste generation and land disposal by encouraging product substitution and materials recovery, recycling, reuse, and treatment.

HSWA has three waste minimization requirements that have been promulgated as regulations under RCRA:

- Hazardous waste generators must submit waste minimization information as part of the biennial reports.
- Generators must certify on the manifest that they have a waste reduction program in place.
- Treatment, storage, and disposal facilities (TSDFs) must certify, at least annually, that they have a waste reduction program in place.

Shell is both a generator and a permitted treatment, storage, or disposal facility (TSDF) and is, thus, required to have a waste reduction program and to submit waste minimization information as part of their biennial reports.

Any waste minimization issues addressing RCRA requirements at Shell are presented in the RCRA media report.

ON-SITE INSPECTION SUMMARY

Credentials were presented to Joe Brewster, Manager, Environmental Conservation for Shell. Following a plant safety presentation and a general discussion of plant processes, including byproduct and waste generation/ handling, a general plant tour was conducted. NEIC personnel reviewed pollution prevention related records/documents, inspected process areas, and obtained information from discussions with Shell personnel.

At the corporate level, Shell has committed to EPA's pollution prevention goal of a 50% reduction in toxic chemical releases by 1995. The Roxana refinery is participating in this pollution prevention program.

NEIC personnel reviewed manifests and the biennial hazardous waste reports. Additionally, the records associated with the chemical emissions inventory files were reviewed.

Exit conferences between regulatory and refinery personnel [Appendix] were conducted to discuss preliminary inspection findings. NEIC personnel stressed that final determinations will be made in conjunction with regional and state personnel.

Current Pollution Prevention Activities

NEIC personnel assessed pollution prevention opportunities as part of the other media inspections. Through this assessment it is apparent that Shell has taken advantage of numerous pollution prevention opportunities created

by regulatory and monetary incentives. Current activities and pollution prevention initiatives, divided by media, are listed in Table 1.

Table 1

CURRENT POLLUTION PREVENTION ACTIVITIES
Shell Oil Refinery
Roxana, Illinois

Activity	Pollution Prevention Initiative
AIR	
Hydrocarbon emissions from pumps and compressors	Replaced older pumps with mechanical or double seal pumps
SOLID WASTE	
Degreasing	Substitution of less flammable degreasing compounds
Spent caustics	Sent off-site to be used as a raw material
Spent catalyst	Sent off-site to be used as a raw material
Slop oil emulsion	Installed new DAF pump
Primary solids from the Wastewater Treatment Plant	Blend with catalytic cracker slurry to produce hazardous waste fuel
DAF floats	Installed new DAF pump
WATER	
Spent caustic	Reused in WWTP neutralization system

Shell establishes annual environmental goals which include annual reductions of 5% for solid waste generation. This goal is tracked by the environmental staff and progress is published monthly in a newsletter to all Shell employees.

Shell is establishing a team, made up of representatives from throughout the facility, responsible for tracking and educating employees on pollution prevention projects. The team, Building Environmental and Safety Traditions (BEST), is currently being formed and the responsibilities are being finalized, but may include:

- Providing communication and training employees
- Serving as a focal point for identification of pollution prevention opportunities and submitting the ideas to the right individuals for action
- Monitoring/tracking pollution prevention progress
- Recognizing significant employee accomplishments
- Encouraging pollution prevention both at work and at home

Shell conducts periodic assessments to see if capital investments needed for a pollution prevention project are economically feasible. The facility generates a "Waste Tracking and Opportunity Assessment" report, which tracks waste generation, and the progress made in reducing the amount of waste generated. Shell is a member of the Industrial Materials Exchange Service where waste streams that are candidates for off-site recycling by other companies are listed.

Potential Pollution Prevention Opportunities

The potential pollution prevention opportunities presented in Table 2 were developed based on inspectors' observations and review of the areas of noncompliance and concern discussed in each media report.

Table 2

POTENTIAL POLLUTION PREVENTION OPPORTUNITIES
Shell Oil Refinery
Roxana, Illinois

Activity	Potential Modification
Stormwater detention area	Upgrade system to prevent overflows
Pitch/refinery fuel gas system	Upgrade system to reduce SO_2 emissions
Heaters and furnaces	Improve instrumentation to reduce excess air which will reduce NO_x emissions
Cooling tower sludge	Discontinue use of chromium treatment in cooling towers
Cooling tower emissions	Discontinue use of chromium in cooling towers
VOC fugitive emissions losses from cooling towers	Use alternative water supply or treat existing source and collect VOCs
VOC fugitive emissions	Update and modify current LDAR program to prevent and reduce VOC emissions

SUMMARY OF FINDINGS

While Shell has undertaken some pollution prevention activities, other opportunities were identified by NEIC. For example, numerous opportunities exist for the reduction of fugitive volatile organic compounds emissions through modifications of the Leak Detection and Repair Program. Discontinuing the use of chromium in the treatment of cooling tower waters will decrease the amount of hazardous waste generated and reduce chromium air emissions.

CLEAN AIR ACT

MULTI-MEDIA COMPLIANCE INVESTIGATION

Shell Oil Company
Wood River Manufacturing Complex
Roxana, Illinois

Facility Address
Shell Oil Company
Wood River Manufacturing Complex
Highway 111
Roxana, Illinois 62084
(618) 255-2478

Investigation Dates

October 25 through November 9, 1993
November 19 through 25, 1993

Investigators

Anne Bevington, EPA-NEIC
Ken Garing, EPA-NEIC
Sergio Siao, EPA-NEIC

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MEDIA REPORT

At the request of EPA Region 5, NEIC conducted a multi-media compliance investigation of the Shell Oil Company - Wood River Manufacturing Complex (Shell) located in Roxana, Illinois. This report, one of a series for the multi-media compliance investigation, discusses investigation findings and addresses air pollution control issues and compliance at Shell.

REGULATORY SUMMARY

Air contaminant emission sources are regulated by the Illinois Administrative Code, Title 35, Subtitle B, Air Pollution, Chapter 1 (IAC), and 35 operating permits [Table 1] issued by the Illinois Environmental Protection Agency (IEPA). Additionally, a Federally Enforceable State Operating Permit (FESOP) for fuel combustion equipment was issued November 2, 1993. A copy of each permit is provided in Appendix A. Shell maintains computer records and calculations to monitor compliance with the operating permit conditions.

Air pollutant emission sources at Shell include: catalytic crackers, process heaters, boilers, sulfur recovery unit (SRU), relief systems, storage tanks, benzene operations, asbestos removal, and fugitive volatile organic compounds (VOCs). Emission limits in the permits have been set for opacity, particulates, sulfur compounds, and VOCs.

Sources of hazardous air pollutants at Shell are regulated by the following National Emission Standards for Hazardous Air Pollutants (NESHAP), 40 CFR Part 61. NESHAP was adopted by the Air Pollution Control Board, by order on December 14, 1978.

Subpart J National Emission Standard for Equipment Leaks of Benzene

Table 1

AIR OPERATING PERMITS
Shell Oil Refinery
Roxana, Illinois

Permit Name	Refinery Designation	IEPA Permit Number	Expiration Date
DU-1	WRR-1	72110615	June 30, 1997
DU-2	WRR-2	72110616	July 31, 1996
Gasoline treaters	WRR-3	72110617	May 31, 1995
Rectified absorber	WRR-4	72110618	June 30, 1997
Gas Plants	WRR-5	72110619	June 30, 1997
Vacuum flasher	WRR-6	72110620	August 31, 1995
CCU-1	WRR-7	72110621	May 17, 1998
CCU-2	WRR-8	72110622	May 17, 1998
Oil recovery	WRR-9	72110623	June 30, 1996
Lube oil deasphalting	WRR-10	72110624	April 30, 1995
Lube fract & extract.	WRR-11	72110625	September 25, 1994
LHT	WRR-12	72110627	November 25, 1995
Asphalt processing	WRR-13	72110626	October 13, 1997
Lubricants compounding	WRR-14	72110628	February 29, 1996
Alkylation	WRR-16	72110630	December 31, 1994
Precursor unit	WRR-17	72110614	August 19, 1998
Benzene extration unit	WRR-19	72110612	August 31, 1995
SMR/HCU	WRR-20	72110611	March 31, 1995
CR-1	WRR-21	72110610	September 17, 1996
Sats gas plant	WRR-22	72110609	April 30, 1995
DHT	WRR-23	72110637	October 31, 1995
KHT-1 & KHT-2	WRR-24	72110636	August 17, 1998
HDU-2/CRU-3	WRR-25	72110635	August 31, 1997
HDU-1/CRU-2	WRR-26	72110634	February 29, 1996
Utilities	WRR-27	72110633	March 31, 1994

Table 1 (continued)

Permit Name	Refinery Designation	IEPA Permit Number	Expiration Date
Dispatching	WRR-28	730100832	January 31, 1994
Cooling water towers	WRR-29	72110631	March 15, 1995
Acetone unit	WRR-31	78040017	June 30, 1998
Open Burning	WRR-32	B9301036	April 16, 1994
Sulfur recovery units/SCOT unit	WRR-38	79090040	June 30, 1994
Catalytic dewaxing unit	WRR-40*	72110624	April 30, 1995
Hartford dock	WRR-41	87120058	August 4, 1997
WWTP sludge dewatering facility	WRR-51	88080051	August 31, 1994
Major effluent treatment project	WRR-52	89020016	March 31, 1994
Caustic vent scrubber (Stauffer)	WRR-53	89030071	March 31, 1994
Fuel Combustion Equipment**	WRR-56	92110025	October 31, 1998

* *Same permit as WRR-10. Both units are combined under one permit with separate WRR files.*
** *Federally Enforceable State Operating Permit (FESOP)*

Subpart M National Emission Standard for Asbestos (Demolition and Renovation)

Subpart V National Emission Standard for Equipment Leaks (Fugitive Emission Sources)

Subpart Y National Emissions Standard for Benzene Emissions from Benzene Storage Tanks

Subpart BB National Emission Standards for Benzene Emissions from Benzene Transfer Operations

Subpart FF National Emission Standards for Benzene Waste Operations

Asbestos removal projects are regulated by 40 CFR Part 61, Subpart M. Asbestos removal projects at Shell are performed by contractors who are subject to contract specifications including complying with the asbestos NESHAP and the state regulations. Contractors must be state certified and are required to make proper notifications prior to the start of any asbestos removal project.

Shell has submitted a waiver application, requesting a time extension until January 1995, for the Subpart FF requirements. The waiver application was submitted to Region 5 in March 1993. At the time of the NEIC inspection, Shell was preparing revisions to the waiver application.

New sources at Shell are regulated by the following New Source Performance Standards (NSPS), 40 CFR Part 60:

Subpart D Standards of Performance for Fossil-Fuel Fired Steam Generators for which Construction is Commenced after August 17, 1971

Subpart J Standards of Performance for Petroleum Refineries

Subpart K,Ka,Kb Standards of Performance for Petroleum Liquid and Volatile Organic Liquid Storage Vessels

Subpart GGG Standards of Performance for Equipment Leaks of VOC in Petroleum Refineries

Subpart QQQ Standards of Performance for VOC Emissions from Petroleum Wastewater Systems

Shell operated a sulfuric acid plant from the 1970s through the late 1980s which was subject to the Subpart H - Standards of Performance for Sulfuric Acid Plants. Operations at this unit were discontinued on August 4, 1989. The operating permit for this unit has expired.

ON-SITE INSPECTION SUMMARY

Credentials were presented to Joe Brewster, Environmental Conservation Manager for Shell. Following a plant safety presentation and a general discussion of plant processes, including byproduct and waste generation/handling, a general plant tour was conducted. Later in the inspection, a more detailed inspection was conducted of process areas, control rooms, air pollution control equipment, sampling locations, and emission points. Figure 1 is a general schematic flow diagram of the refinery. Records/documents associated with the regulated activities were also reviewed. Referenced photographs are contained in Appendix B. Exit conferences between regulatory and refinery personnel [Appendix C] were conducted to discuss preliminary inspection findings. NEIC personnel stressed that final determinations will be made in conjunction with regional and state personnel.

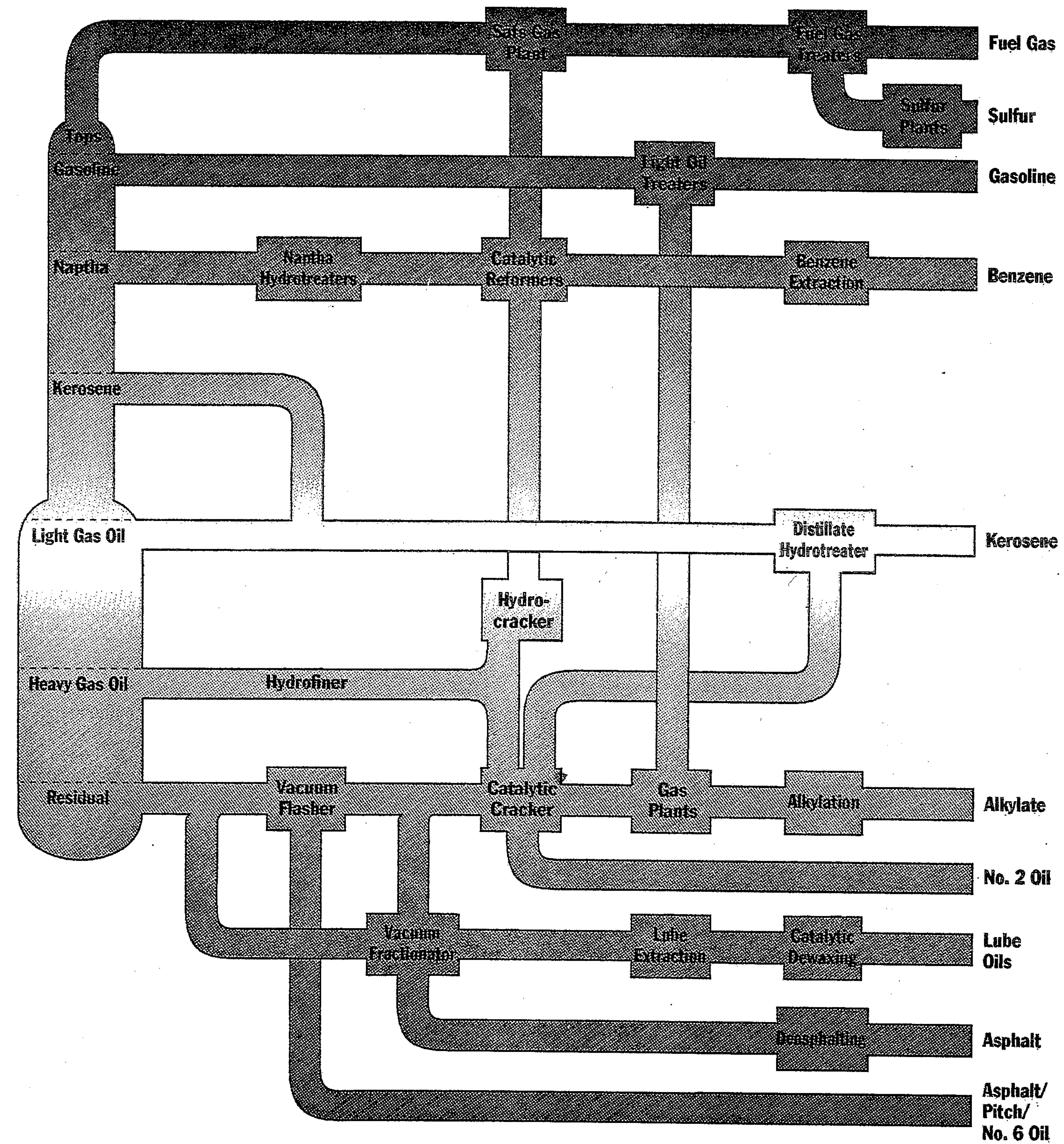

Figure 1
PROCESS FLOW DIAGRAM
Shell Oil Company
Roxana, Illinois

Facility Inspection/Discussions

The Wood River refinery is capable of processing 250,000 barrels (bbls) of crude per day. Crude oil is delivered by pipeline and stored in crude oil tanks with capacities ranging from 950 to 291,000 bbls. Major products from this refinery include: gasoline, jet fuel, diesel fuel, fuel oil, lube oils, and asphalt. These products are stored in tanks ranging in size from 100 to 171,000 bbls.

Major processes used at this refinery include: crude desalting, atmospheric distillation, vacuum distillation, thermal cracking, catalytic cracking, catalytic reforming, hydrotreating, isomerization, alkylation, polymerization, lube oil manufacturing, dewaxing, and desulfurization.

With the exception of the catalytic cracking unit (CCU), the major process units are closed systems and the attendant process heaters are the main emission sources from the process units. Other sources of air emissions include: boilers, sulfur recovery units, relief systems, storage tanks, and fugitive VOCs [photograph 1].

Catalytic Cracking Unit

The refinery operates two CCUs. Particulate, sulfur dioxide (SO_2), carbon monoxide (CO), and opacity emission limits have been established for each CCU. The CCU converts gas oils into lighter products using heat and a catalyst to promote the reaction. The products are drawn off and sent to fractionating columns to separate various products. Catalyst is continuously removed from the reactor and sent to the regenerator portion of the CCU. In the regenerator section, coke and tars which collect on the catalyst during the reaction are burned-off. The regenerated catalyst is collected by a series of cyclones and returned to the reactor. A small quantity of new catalyst is continuously added to the system to make-up for spent catalyst (catalyst fines) which is removed.

The exhaust gases leave the regenerator section through a catalyst fines separator, CO boiler, and an electrostatic precipitator (ESP) for particulate control. The catalyst fines from the separator and the ESP are collected, stored in bins, and sold to cement companies. The CO boiler burns the CO and recovers energy from the exhaust gases.

Particulate emissions from each CCU are controlled by eight primary cyclones located within the regenerator, two parallel sets of four external cyclones, and an electrostatic precipitator (ESP) divided into two parallel cells. Each CO boiler stack is equipped with continuous emission monitor (CEM) for opacity, O_2, CO, and CO_2. When the CO boiler and/or ESP is down for maintenance or during an upset condition, the exhaust gases are vented directly to an auxiliary stack. Each CCU is equipped with an auxiliary stack. Monitoring of auxiliary stack emissions is not conducted; however, a malfunction report is submitted to the IEPA. Six bypass events have been documented on these reports from January 1991 through October 1993, as summarized below:

Date	Unit	CO Released, Tons	TSP Released, Tons
January 10, 1991	CCU-2	50	0.6
July 3, 1991	CCU-2	41	0.52
August 2, 1992	CCU-2	515	2.3
August 26, 1992	CCU-1 & CCU-2	248	46.7
April 23, 1993	CCU-2	0.185	-
April 28, 1993	CCU-2	656	2.9

At the time of the inspection, the opacity measurements for CCU-1 and CCU-2 were 22% and 23%, respectively. The emission data observed during the NEIC inspection for the CCUs are as follows:

	CCU-1	CCU-2
Opacity	22%	23%
O_2	0.03%	0.09%
CO	2.9%	9.0%
CO_2	14.0%	12.2%

The combined sulfur dioxide limit for the two CCUs must not exceed 3,430 pounds per hour [35 IAC 214.382(c)(3)(I)]. SO_2 emissions from each CCU are calculated by summing the sulfur emissions from three sources: refinery fuel gas combusted in the CO boiler, sulfides in the sour water sprayed into the regenerator, and the sulfur on the burned coke. Records are maintained for the fuel usage with sulfur content, sour water usage, and coke burned. Shell also maintains records of the daily computer calculated SO_2 emissions. The SO_2 emissions are calculated daily and the results are submitted quarterly. A review of the quarterly SO_2 reports is presented in the "Records Review" section of this report.

Particulate stack tests, conducted in January 1993, indicated a particulate emission rate of 0.0174 grains per dry standard cubic feet (gr/dscf) for CCU-1 and 0.0447 gr/dscf for CCU-2 [Appendix D]. Soot blowing operations were not conducted for the testing period. Soot blowing operations are conducted four times per day; however, none occurred during the stack tests. The particulate test emission rate from each CCU are less than the allowable emission rates.* On one test run for CCU-2, the emission rate was determined to be 72.9 pounds per hour (lbs/hr) versus the allowable rate of 78.9 lbs/hr.

---

* *Calculated allowable emission rate is* $E = [55.0 \; x \; (P)^{11}]-40$
Where E = allowable Emission rate and P = Catalyst recycle rate in tons per hour

Emission rates on the other test runs were a factor of 4 or 5 less than the allowable emissions.

Prior to 1993, stack tests were conducted on a quarterly basis; however, as a cost cutting measure stack tests are to be conducted annually.

Process Heaters and Boilers

The refinery operates 59 process heaters ranging in size from 5 to 454 million Btu (MMBtu) per hour. There are five boilers ranging in size from 249 to 700 MMBtu per hour. A listing of the heaters and boilers, heat capacities, fuels burned, and installation dates is contained in Appendix E. Five heaters and two boilers are subject to the NSPS requirements [Table 2].

Refinery fuel gas (RFG), refinery fuel pitch (RFP), and natural gas are used to fire the refinery heaters and boilers. RFG is produced within the refinery by cleaning (removal of H_2S and other impurities) the cracked gas produced in various process units. A schematic diagram of the RFG system is provided in Figure 2. RFP produced from the Vacuum Flasher Units is stored in tank A-48 [Figure 3]. RFP is withdrawn from A-48, circulated through two supply headers, and distributed to the various process heaters and boilers. RFP must be continually circulated through the headers to ensure that the fuel remains in a pumpable state. Natural gas is supplied by a contractor. Natural gas is blended with the RFG or can be sent directly to the heaters.

The RFP was sampled during the NEIC inspection. A 450 °F sample of the RFP was taken from the location shown in photograph 2. The sample was analyzed by NEIC for total sulfur content by X-ray fluorescence spectroscopy using ASTM Method D2622. Sulfur content of the collected sample was found to be 1.83% which is below the regulatory limit of 3%.

Table 2

NSPS HEATERS AND BOILERS
Shell Oil Company
Roxana, Illinois

Process Unit	Start-Up Date	Type of Fuel	State Permit[1] SO_2 Limit (lbs/hr)	Remarks
VFU[2]-North	May 23, 1986	RFG[3]/RFP[4]	378	40 CFR 60 Subpart J
VFU-South	May 23, 1986	RFG/RFP	378	40 CFR 60 Subpart J
Catalytic Dewax Heater	March 21, 1988	RFG	[5]	40 CFR 60 Subpart J
Acetone Converter[6] Heater H-1	May 19, 1980	RFG	[7]	40 CFR 60 Subpart J
Acetone Converter[6] Heater H-2	May 19, 1980	RFG	[7]	40 CFR 60 Subpart J
Boiler No. 17	October 1974	RFG/RFP	2,400	40 CFR 60 Subpart D
Boiler No. 18	December 1979	RFG/RFP	2,400	40 CFR 60 Subpart J

1 *Based on total SO_2 for Source Operating Group containing listed heater or boiler*
2 *Vacuum Flashing Unit*
3 *Refinery Fuel Gas*
4 *Refinery Fuel Pitch*
5 *No SO_2 limit specified in permit for the combustion gas. Permit states that H_2S concentration of RFG shall be not exceed 0.10 grains/dscf.*
6 *Heater out of service since 1990*
7 *No SO_2 limit specified for the combustion gas, nor a limit of SO_2 stated for the RFG.*

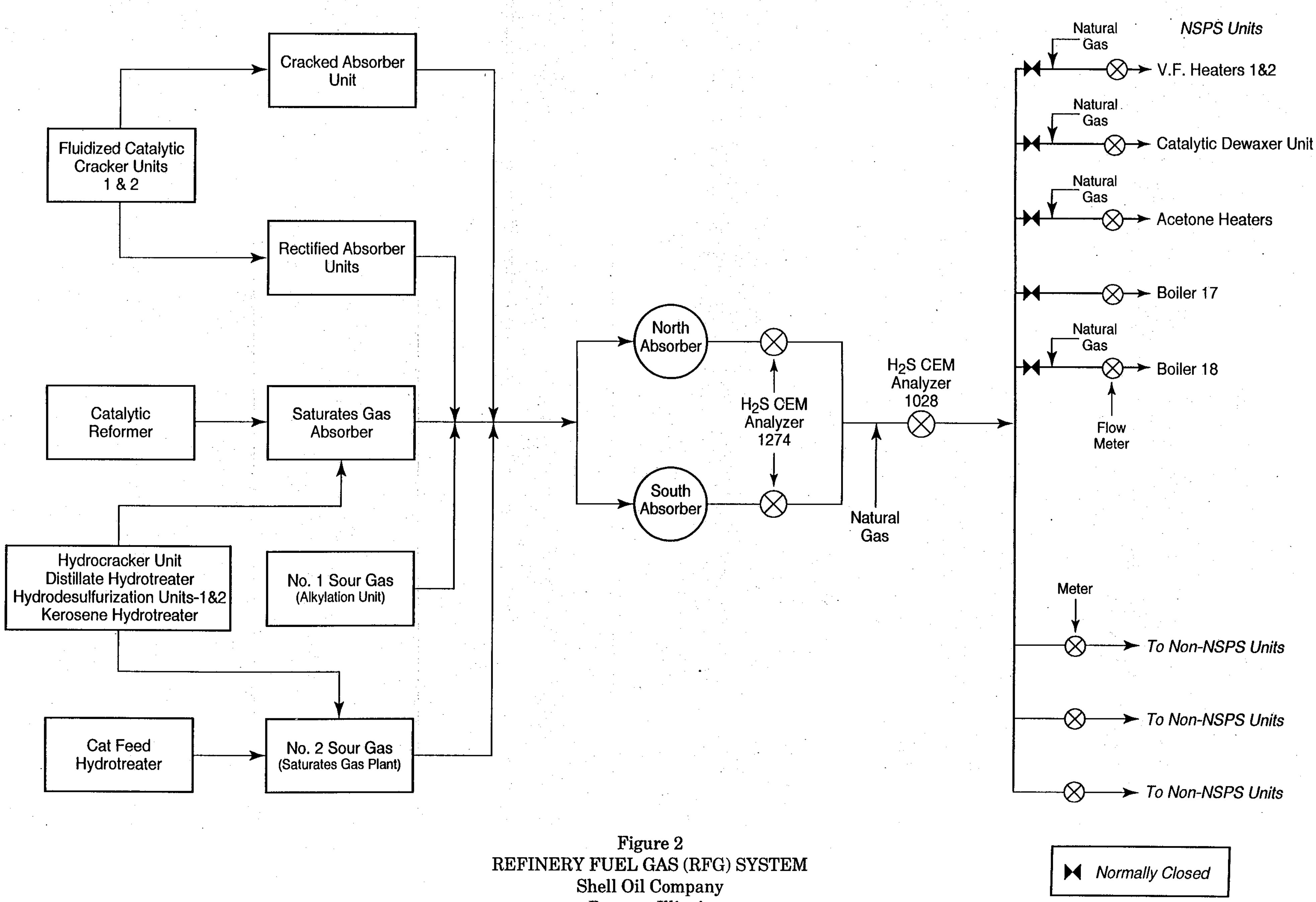

Figure 2
REFINERY FUEL GAS (RFG) SYSTEM
Shell Oil Company
Roxana, Illinois

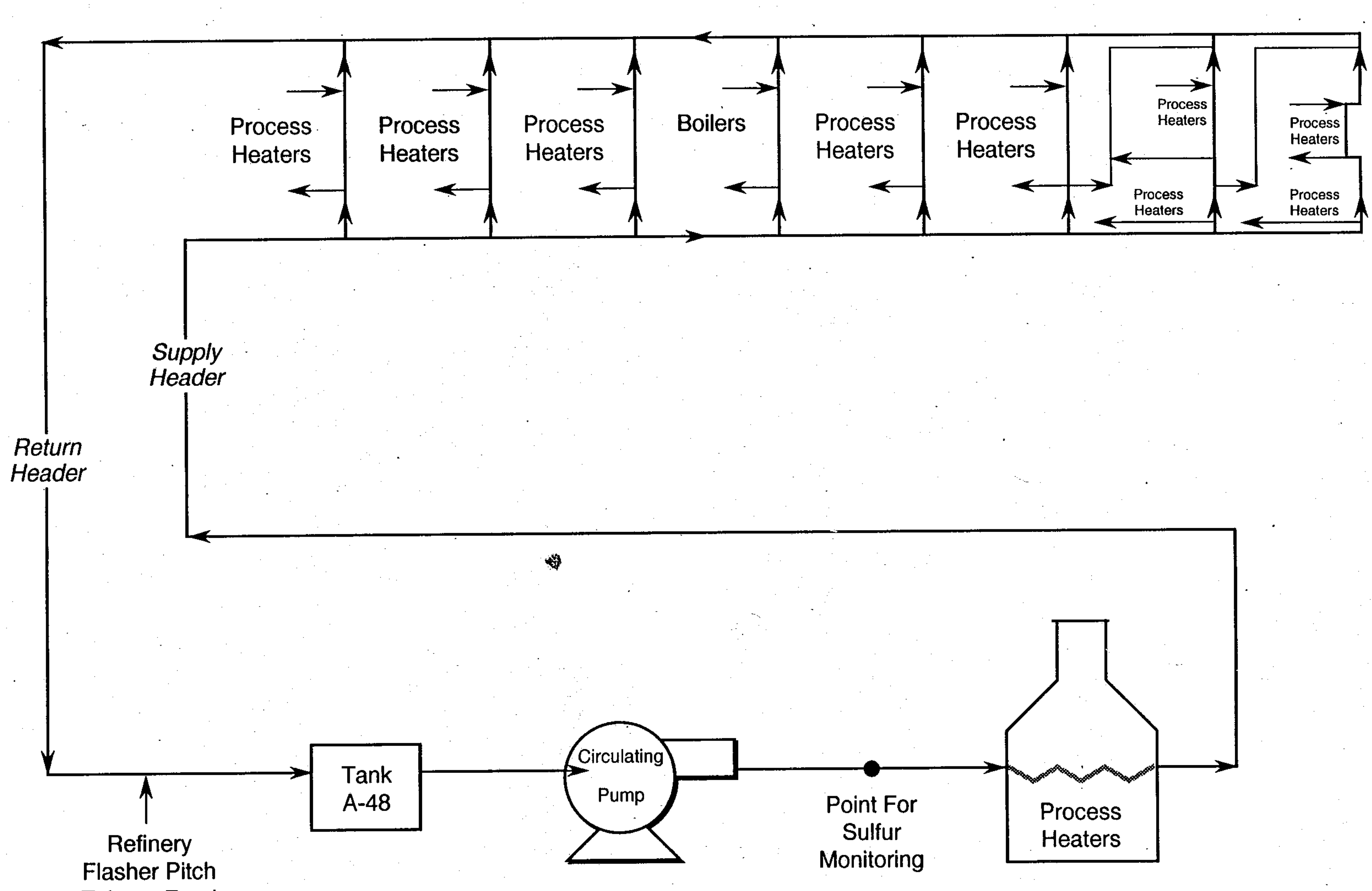

Figure 3
Refinery Fuel Pitch Schematic Diagram
Shell Oil Company
Roxana, IL

The piping and instrumentation drawings (PIDs) show that the north and south vacuum flasher heaters have the capability of burning RFP and/or RFG [Appendix F]. If RFP is burned, fuel usage is calculated by taking the difference between the quantity of RFP entering and leaving the vacuum flasher fuel circulating loop. When RFP is not burned, the vacuum flasher fuel circulating loop is filled with a flushing oil. During the NEIC inspection, RFG was burned in both vacuum flasher heaters. Refinery fuel pitch had been removed from the vacuum flasher fuel circulating loop and replaced with flushing oil. Quarterly NSPS emissions reports indicate that RFP has not been burned in these heaters since October 1, 1990.

The catalytic dewaxing heater PID shows that this unit does not have the capability to burn RFP. This heater has the capability of burning RFG or natural gas. Quarterly NSPS emissions reports indicate that RFG has not been burned in these heaters since October 1, 1990.

The two acetone converter heaters have been out of service since 1990. Gina Nicholson, Senior Engineer for Shell, indicated that this unit only has the capability of burning RFG.

Boilers 18 and 17 have the capabilities of burning either RFG or RFP. Quarterly NSPS emissions reports indicate that RFP has not been burned in boiler 18 since October 1, 1990. Quarterly NSPS reports for boiler 17 indicate that RFG was burned from the fourth quarter 1992 through first quarter 1993. RFP and RFG were burned in boiler 17 during the second and third quarters of 1993.

Although several of the NSPS units (Vacuum Flasher Heaters 1 and 2, Catalytic Dewaxer, and boiler 18) are connected to the RFG system, only natural gas is used to fire these heaters. For these units, the RFG supply line

has been blocked (not removed) and only natural gas is routed to the heaters. There is no mechanism to monitor or provide notification in the event that natural gas use is curtailed, thus, requiring the use of RFG.

Shell personnel do not consider boiler 17 to be an NSPS boiler when RFP is used either as the primary or supplemental fuel [Appendix G]. Shell considers RFP to be a nonfossil fuel and, therefore, considers the NSPS requirements to be nonapplicable. This opinion is based on information provided in 1975 correspondence [Appendix H] between Region 6 and the Shell Deer Park, Texas refinery. This correspondence indicates that RFP is a non-fossil fuel. This determination was based on information regarding derivation and composition specifically pertaining to the Deer Park refinery. The Wood River refinery has not requested a determination by Region 5 regarding the designation of RFP as a nonfossil fuel. Because the Wood River refinery RFP is derived from petroleum "for the purpose of creating useful heat"* and has not been designated a nonfossil fuel, the Wood River RFP should be considered a fossil fuel and the boiler should be considered an NSPS source.

The NSPS opacity limits for boiler 17 are 20%; however, refinery personnel stated that they consider the opacity limit to be 30% when RFP is burned. Since fourth quarter 1991, RFP has only been burned in boiler 17 during the second and third quarters of 1993. A review of the boiler 17 NSPS opacity reports is presented in the "Records Review" section of this report.

The IEPA regulations establish limits on the sulfur content in the RFG and RFP. RFG supplied to heaters and boilers which are not NSPS equipment is limited to no more than 39 grains H_2S/100 dscf in a 3-hour rolling average. A limit of 10 grains H_2S /100 dscf is required for the NSPS heaters and boilers.

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* *Wording provided from 40 CFR 60.41(b)*

The sulfur content of the RFP is limited to 3% weight sulfur. Review of the sulfur content for RFG and RFP is discussed in the "Records Review" section of the report.

The H_2S content in the RFG is monitored using an H_2S analyzer at the Cracked Gas Plant. Compliance with the H_2S limit is determined by an H_2S Continuous Emission Monitor (Shell Analyzer No. 1028) located downstream of the absorbers [Figure 2]. This analyzer is used for compliance for both the 10 and 39 grain limits, with separate alarms to indicate when either value is exceeded. Additionally, as a reference check, an H_2S analyzer (Shell Analyzer No. 1274) also monitors the H_2S content in the gas exiting the north and south absorbers [Figure 2]. When using the H_2S analyzer, compliance with the 39 grain limit is based on a 3-hour rolling average. The H_2S analyzer calculates the 3-hour average. As an alternative to the H_2S analyzer, H_2S content can be analyzed every 8 hours using the Tutwiler Method. If the Tutwiler Method is used, compliance is based on each sample result.

In addition to sulfur limits on the RFG and RFP, the IAC regulations establish limits on the quantity of SO_2 emitted from refinery heaters and boilers. The refinery has been divided into 10 source operating groups (SOGs) with established SO_2 limits [Table 3]. SO_2 emissions are calculated using quantity of fuel burned and the associated sulfur content. The amount of gas and/or pitch burned and sulfur content is recorded hourly. From these data, the SO_2 emissions are calculated hourly for use in preparing the quarterly reports. The SOG SO_2 are established in IAC 214.382(c)(3) and have also been included in the appropriate air permits.

Table 3

SOURCE OPERATING GROUP (SOG) SO_2 LIMITS
Shell Oil Refinery
Roxana, Illinois

Name	Regulated Heaters/Boilers	SO_2 Limit [1] (pounds/hour)
Distillation Unit No. 1	DU-1 Primary Heater, DU-1 Secondary Heater	459
Distillation Unit No. 2	West vacuum flasher heater, East vacuum flasher heater, Lube crude heater, East mixed crude heater, West mixed crude heater	1,260
Flasher	(2) VF-1 heaters, (2) VBU heaters, Visbreaker flasher heater, Refinery fuel pitch heater	378
Cracked Gas Plant	RA deethanizer heater, RA debutanizer heater, CAU rich oil still heater	159
Alky/BEU/CFH	CFH heater, Alky no. 2 heat medium heater, ARU1 heat medium heater, ARU2 heat medium heater	346
Aromatics West	(3) HCU heaters (6) CR-1 heaters SGP heater	1,660
Aromatics East	(4) CR-3 heaters DHT heater HDU-2 heater	768
Boiler House	Boilers [2] 9, 10, 11, 12, 13, 15, 16, 17, and 18	2,400
Cracking	CCU1, CCU2, and heaters	3,430
Overall [3]	DU-1 SOG, Aromatics East SOG, Boiler house SOG, Cracked gas plant SOG	2,710

1 *SO_2 limit are applied to any petroleum refinery in the Village of Roxana as established in IAC 214.382(c)(3).*

2 *Boilers 9, 10, 11, 12, and 13 have been taken out of service.*

3 *Name provided by refinery personnel.*

Sulfur Recovery System

The sulfur recovery system [Figure 4] consists of the North and South H_2S absorbers, a sour water stripper, three Claus trains [sulfur recovery units (SRU) A, C, and D], and a Shell Claus Off-gas treater (SCOT). The sulfur recovery capacity is 450 long tons per day (LTD). Normally, all three trains are in operation, but two trains can handle normal production if one train is down for maintenance.

The absorbers remove H_2S from the major sour (high in H_2S) fuel gas streams by using an aqueous diethanolamine (DEA) solution. The DEA absorbs H_2S, carbonyl sulfide (COS), carbon dioxide (CO_2) via countercurrent contact. The absorbed compounds, primarily H_2S, are removed at the SRUs and the DEA is regenerated for reuse. The North absorber treats low pressure sour refinery fuel gas and the South absorber treats high pressure sour refinery fuel gas.

Prior to treatment, the sulfur rich DEA feed (fat DEA) from the North and South absorbers are combined with fat DEA from the nearby Clark refinery and Amoco facility. Contractual arrangements between Shell and the other two companies require that Shell be responsible for cleaning the fat DEA and returning a clean DEA (lean DEA) solution. The fat DEA from the two companies is mixed with the Shell fat DEA. During the NEIC inspection, approximately 800 gpm of fat DEA from Shell, 400 gpm of fat DEA from Clark, and 25 gpm of fat DEA from Amoco were being treated. Shell employees estimated that approximately 250 LTD of sulfur are recovered, with 175 LTD contributed by Shell, 70 LTD contributed by Clark, and 5 LTD contributed by Amoco.

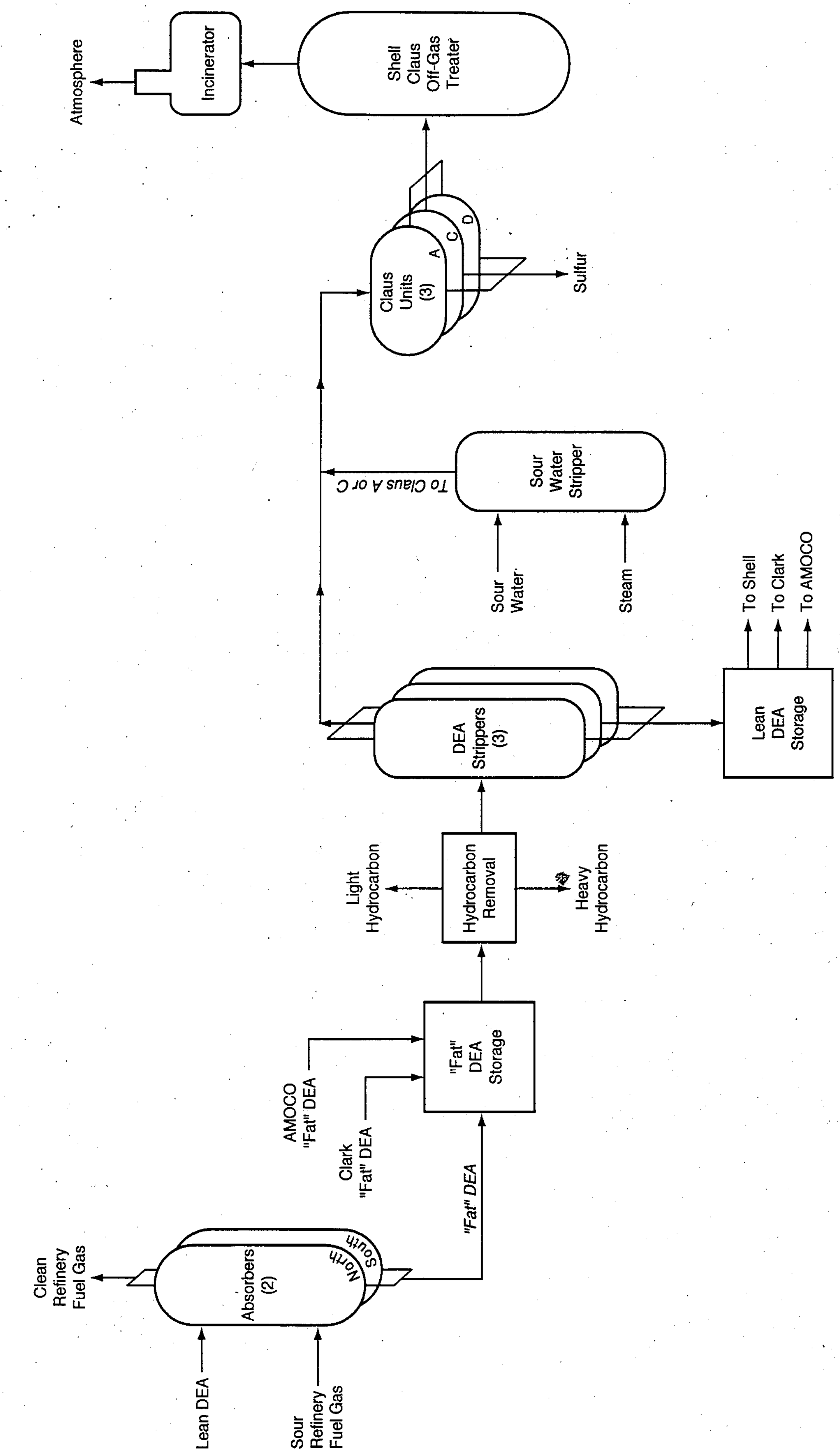

Figure 4
H_2S PROCESSING SYSTEM
Shell Oil Company
Roxana, Illinois

The fat DEA passes through a hydrocarbon removal process prior to entering the strippers [Figure 4]. Light hydrocarbons are vented to the incinerator and heavier hydrocarbons are removed by vacuum truck. The hydrocarbon-free DEA enters one of three independently operated strippers. Within the strippers, hot gases strip the H_2S and other absorbed materials from the DEA. Lean DEA collected from the stripper bottom is temporarily stored before reuse at Shell, Clark, or Amoco. The condensed overhead vapors from the stripper are fed to the Claus units for sulfur removal.

Large quantities of hydrocarbons entering with the DEA may cause upsets within the sulfur recovery system. Paul Pizzini, Process Engineer, indicated that, occasionally, hydrocarbons have passed through the hydrocarbon removal process. The hydrocarbons pass through the stripper, exit with the overheads vapors, and contaminate the Claus units.

An additional feed source to the Claus units include vapors from the sour water stripper. The sour water stripper removes H_2S and ammonia (NH_3) from various refinery sour water sources. Steam is injected into the stripper column which strips the H_2S and NH_3. The overhead vapors are condensed and returned to the stripper column. The noncondensed vapors, containing the H_2S and NH_3, are directed to the Claus units.

The Claus units convert the sulfur compounds into elemental sulfur. Each Claus unit consists of a thermal reactor and two catalytic reactors. The Claus trains partially oxidize H_2S to SO_2, which reacts with H_2S in the presence of a catalyst to form elemental sulfur and water. The Claus units operate at a conversion efficiency of about 92%. The elemental sulfur is collected in a sulfur pit, then sold. The tail gases from the Claus trains contain about 8% by volume of reduced sulfur compounds and are fed to the SCOT unit.

The SCOT unit converts SO_2 and other sulfur compounds to H_2S. Tail gases from the Claus unit are heated and combined with hydrogen. The SCOT reactor contains a catalyst which promotes the conversion of sulfur compounds to H_2S. The H_2S is removed via selective absorption using methyl-diethanolamine and routed back to the Claus trains. The gases leaving the absorber pass through one of two incinerators converting the H_2S to SO_2 before exiting the stack [photograph 3].

During the NEIC inspection, SO_2 emissions were typically less than 250 ppm. The tail gas emissions are emitted through one of two stacks. A CEM monitors SO_2 concentrations from each stack. The average of the two readings is used to calculate SO_2 emissions and is reported on the quarterly reports.

<u>Relief Systems</u>

The majority of process unit pressure relief valves (PRVs) are connected to one of six flare systems [Table 4]. Each flare, except the high pressure flare, is equipped with a compressor to recover hydrocarbons. Hydrocarbons recovered by the compressors are discharged to the maintenance dropout tanks (MDOs). Hydrocarbons removed from the MDOs are reprocessed throughout the refinery.

The flares have a 2-pounds-per-square-inch gauge (psig) water seal to keep the vented gases flowing to the recovery compressors. When emergency situations arise that require a rapid release of liquids and gases from a unit, the water seal is broken and the excess gases are combusted in the flare.

Table 4

FLARE EMISSION SOURCES
Shell Oil Refinery
Roxana, Illinois

Flare Name	Process Unit Discharge Sources
High Pressure Hydroprocessing (North)	Distillate hydrotreater, steam methane reformer, hydrocracker, catalytic reformer No. 1, saturates gas plant
Low Pressure Hydroprocessing (South)	Hydrodesulfurization No. 1, hydrodesulfurization No. 2, catalytic reformer No. 2
Distilling	Distillation No.1, vacuum flasher No. 1, vacuum flasher No. 3, catalytic cracker Nos. 1 and 2
Ground flare	Cracked gas plant, rectified absorber
Alkylation	Catalytic cracker No. 1, catalytic cracker No. 2, catalytic feed hydrotreater, benzene extraction, kerosene hydrotreater, alkylation
Lube	Catalytic dewaxing unit,* DAU,* LFE

* *Designates NSPS process unit*

Two process units, the catalytic dewaxing unit (CDU) and the deasphalting unit (DAU), are subject to NSPS requirements. Therefore, the flares servicing these units are also subject to the NSPS requirements of 40 CFR § 60.18.

The NSPS flare requirements include operating the flare with a flame present at all times and monitoring with a thermocouple or any equivalent method to detect the presence of a flame. Each Shell flare is equipped with thermocouples and a television monitor to observe the pilot flame. Infrared cameras also monitor each flare with the exception of the distilling flare. An alarm is activated in the control room if the pilot flame is extinguished.

Approximately 111 PRVs, located in 18 processing units, vent directly to the atmosphere [Appendix I]. As required by Illinois Air Code Section 215.144, the refinery submitted a report to IEPA listing 10 excessive releases during the 3-year period September 1, 1990 through September 1, 1993 [Table 5].

The number of excessive releases from safety relief valves is limited to no more than three in any 12-month period [35 IAC 215.144]. On five occasions the number of excessive organic releases from safety relief valves has exceeded three in any 12-month period.

Storage Tanks

Storage tanks at the refinery range in size from 10 to 291,000 bbls and are used to store a variety of hydrocarbon materials. The more volatile materials are stored in tanks equipped with internal and external floating roofs. Appendix J lists refinery storage tanks, along with stored material, tank type, capacity, and throughput. NSPS storage tanks, benzene storage tanks, and waste benzene storage tanks are listed in Table 6 and are shown in Figure 5. Estimated emissions from the storage tanks [Appendix K] are computer calculated by Shell using EPA published emission factors (AP-42) and include breathing, working, standing, and withdrawal losses. The tanks are located in three primary tank farms: West, Southwest, and North Property tank farms.

Shell personnel conduct primary and secondary seal inspections monthly for the floating roof tanks and NSPS tanks located at Shell. The IEPA inspectors also conduct random seal gap inspections to audit company results. Results of the inspections are maintained in a computer summary by Shell and are available to inspectors when requested. NEIC reviewed the Shell

Table 5

1990 THROUGH 1993 SAFETY RELIEF VALVE REPORT
Shell Oil Refinery
Roxana, Illinois

Date	Safety Relief Valve Set	Duration of Release (Minutes)	Quantity of Excess Release (lbs of H_2S and Mercaptans)
18-Sep-90	Distilling unit No. 2 Depropanizer column	0.5	80
22-Dec-90	Hydrodesulfurizer No. 2 Stripper vent gas column	3.5	200
1-Jan-91	Cracked gas plant RAU Debutanizer	36	140
23-Jun-91	Distilling unit No. 1 Debutanizer column	25	35
8-Jul-91	Catalytic reformer No. 1 Chloride absorber	10	1.8
27-Jan-92	Sats gas plant Debutanizer column	25	80
9-Mar-92	Lube Hydrotreater KO Pot	2	14
18-Oct-92	Distilling unit No. 2 Depropanizer column	10	1,230
26-Jan-93	Hydrodesulfurizer No. 2 Stripper vent gas column	0.25	9
23-Feb-93	Sulfur plant sour water stripper	20	280*

* *This release did not contain any organic material*

Table 6

VOC STORAGE TANK DATA
Shell Oil Refinery
Roxana, Illinois

Tank Number	Product stored	Vapor Pressure (psia)[1]	Capacity (bbls)	Vapor controls	Remarks
A-62	Benzene	1.772	54,400	Single seal, internal floating roof	40 CFR Part 61 Subpart Y
A-63	Benzene	1.772	54,400	Single seal, internal floating roof	40 CFR Part 61 Subpart Y
A-64	Benzene	1.772	54,400	Single seal, internal floating roof	40 CFR Part 61 Subpart Y
A-149	Wastewater	.35	171,429	Double seal, external floating roof	40 CFR Part 61 Subpart FF
A-150	MTBE	4.0	5,000	Double seal, internal floating roof	40 CFR Part 60 Subpart Kb
A-151	MTBE	4.0	5,000	Doble seal, internal floating roof	40 CFR Part 60 Subpart Kb Not yet in service
B-121	Slop oil/water	1.0	860	Vents to flare	40 CFR Part 60 Subpart QQQ
CH-290	Sulfolane wastewater	1.0	2,500	Double seal, external floating roof	40 CFR Part 61 Subpart FF
D-52	Slop oil/water	1.0	210,000	Fixed roof Vents to flare	40 CFR Part 60 Subpart Kb
D-53	Slop oil/water	1.0	210,000	Fixed roof Vents to flare	40 CFR Part 60 Subpart Kb
D-54	Slop oil/water	1.0	210,000	Fixed roof Vents to flare	40 CFR Part 60 Subpart Kb

[1] *pounds per square inch, absolute*

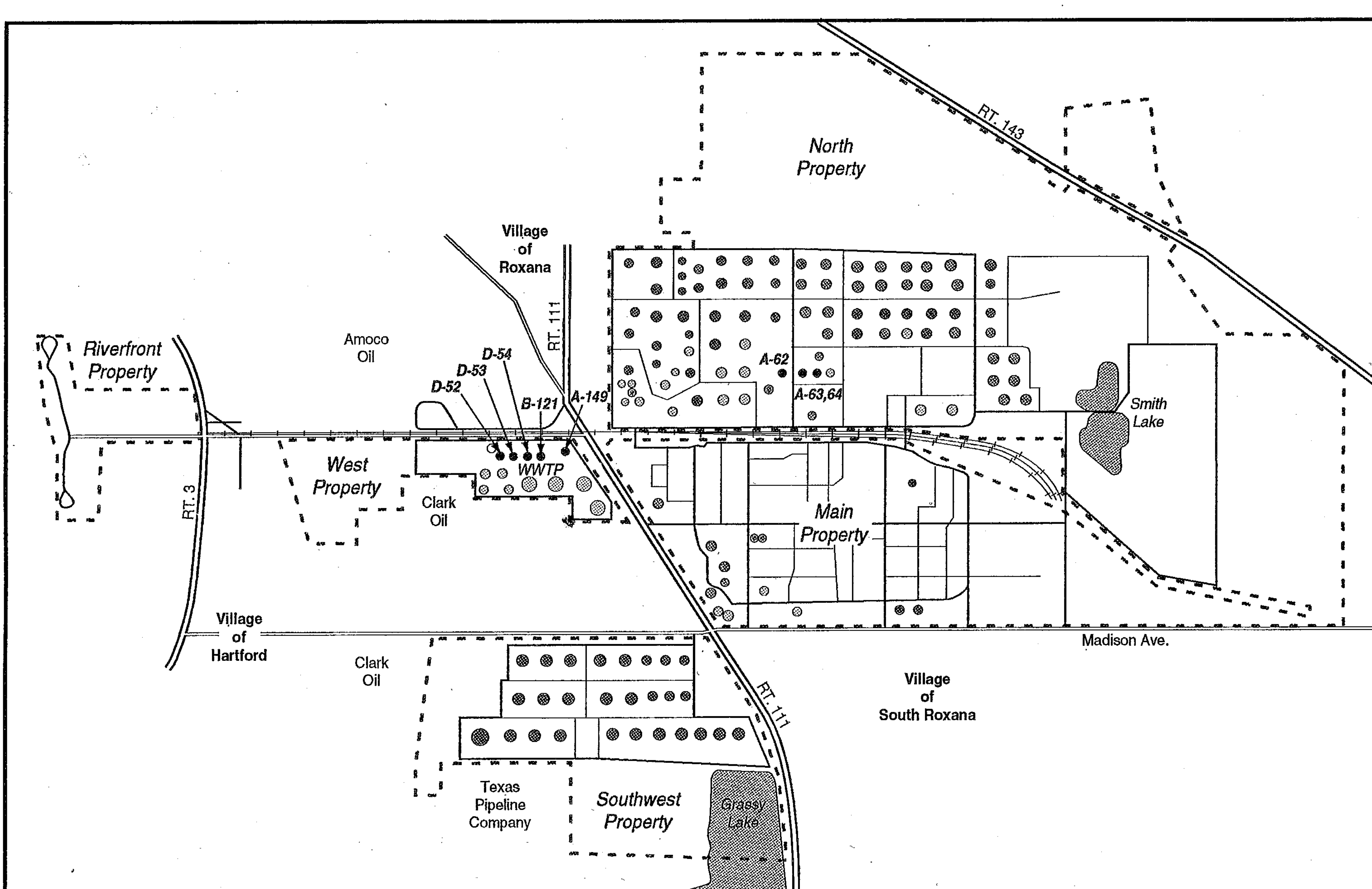

Figure 5
TANK STORAGE LOCATIONS
Shell Oil Company
Wood River Manufacturing Complex
Roxana. Illinois

inspection records and did not measure seal gaps. Appendix L contains the inspection report summaries and seal maintenance records obtained during the NEIC inspection. If seal gaps are identified or maintenance is needed, the tank field supervisor is notified. After the problems are corrected, the tank is re-inspected.

Benzene Waste Operations

The effective date of the NESHAP for benzene waste operations (40 CFR Part 61, Subpart FF) was stayed until final action was taken on clarifying amendments. The final rule was published January 7, 1993 with a compliance date of April 7, 1993.

In anticipation of the requirements, Shell had conducted a survey and testing program to determine the quantities of benzene in the refinery waste streams. The total annual benzene (TAB) quantity in the waste streams was estimated to be approximately 107 mega grams per year (Mg/yr), subjecting the refinery to the Subpart FF requirements.

NEIC collected samples of desalter water and the combined feed to the wastewater treatment plant (WWTP) for comparison to Shell's reported values. NEIC analytical results indicated 10 ppm for the desalter water and 4.7 ppm for WWTP feed. The NEIC results are within the ranges reported by Shell.

Remediation groundwater extracted for use in the refinery cooling towers is contaminated with benzene. Several wells are used to extract the contaminated groundwater with benzene concentrations ranging from 0 to 52 ppm [Appendix M]. Based on the large flows (approximately 3,400 gpm combined flow) the amount of benzene contained in the extracted water is about 94,800 pounds.* The benzene in the extracted groundwater does not need to be included in the TAB; however, the water streams containing more than 10 ppm benzene must be controlled in accordance with Subpart FF. Benzene control measures for the well water streams containing greater than 10 ppm benzene were not included in the Application for Waiver of Compliance.

Shell submitted an Application for Waiver of Compliance for this subpart in March 1993. The application identified a final compliance date of January 7, 1995. NEIC and Region 5 personnel discussed portions of the application with refinery personnel. During these discussions, modifications and additions to the proposed control plan were identified. Eric Petersen, Process Engineer for Shell agreed to formalize these modification/changes and provide the information to Region 5 as part of an updated waiver application.

Asbestos Removal Projects

Shell has an ongoing survey to identify the amount and areas where asbestos containing materials (ACM) are present. Mark Cain, Asbestos Supervisor, indicated 40% of the refinery has been assessed. Each process unit is divided into operating areas and sampled to determine if ACM is present. Areas are then prioritized for removal scheduling.

Large asbestos removal projects at Shell, including emergency removals, are performed by contractors who are subject to contract specifications and must comply with the asbestos NESHAP and state regulations. The contractors must be state certified and are required to make the proper

* *As a result of the contaminated groundwater, 94,800 pounds of benzene were reportedly released from the cooling towers. Information reported in 1992 on the EPCRA Form R submittal*

notifications. A third party, Safety Environmental, is contracted to conduct the air monitoring for each project. The removal contractor maintains the notifications, permits, and monitoring data on-site during an active project.

Small asbestos removals are conducted by Shell's asbestos team. The asbestos group is responsible for taking samples of potential ACM upon request from the process unit operators. Before any maintenance or demolition work is conducted, the asbestos team determines if a removal is necessary.

During the NEIC inspection, an asbestos removal and encapsulation project was completed. An inspection of a small removal area in CCU-1 was conducted on November 1, 1993. UE&C Catalytic, an asbestos contractor, was removing approximately 300 linear feet of ACM. The project was in the final clean-up phase, and only a small enclosure was still in place [photograph 4]. Proper notifications were made and contractor and worker licenses were up-to-date. The asbestos was double bagged in 6-mil plastic and transferred to an asbestos disposal roll-off. The roll-off was marked with asbestos labels.

Removal notices, Notices of Intent to Remove and Dispose of Asbestos, and annual removal notices from January 1991 to October 1993 were reviewed and no deficiencies were noted. Small abatement jobs (less than 160 linear feet) required for routine maintenance and repairs are covered on a blanket notification submitted to IEPA annually. Contractors are responsible for large asbestos removals, encapsulations, and emergency repairs. Shell employs 26 certified asbestos workers and 12 workers with contractor/supervisor training. The work performed by contractors is supervised and inspected by Shell personnel holding asbestos supervisor certification.

Fugitive Volatile Organic Compound Emissions

Monitoring Requirements

Fugitive VOC emissions are regulated by 40 CFR Part 60 Subpart GGG (Standards of Performance for Equipment Leaks of VOC at Petroleum Refineries), 40 CFR Part 61 Subpart J (National Emission Standards for Equipment Leaks of Benzene), and IAC Sections 219.445 through 219.448. Subpart GGG establishes VOC monitoring requirements for refinery equipment constructed or modified after January 4, 1983; Subpart J establishes requirements for fugitive emissions from equipment in benzene service. The standards establish identification, monitoring, and recordkeeping requirements for pumps, compressors, and valves which handle hydrocarbons having an initial boiling point greater than 150 °C.

The NSPS and Benzene NESHAP regulations require each valve, pump, and compressor in VOC service to be identified with a unique identification code and to be monitored on a routine basis using procedures specified in EPA Reference Method 21.*

The Shell leak detection and repair (LDAR) program monitors approximately 55,000 equipment components. Shell monitors 2,600 components in benzene service and 1,300 components in NSPS service. Remaining components are monitored under the state fugitive emissions program. Identification tags have been attached to VOC valves [photograph 5]. All tags display the plant process number and the component number. A computer log is maintained which lists all monitored components by process unit.

* *As specified in 40 CFR Part 60 Appendix A*

The Shell LDAR program is conducted by Shell personnel. Operators from each process unit are responsible for monitoring the appropriate valves in their unit. Hundreds of different operators are potentially responsible for LDAR monitoring.

Follow-up repairs for leaking components are initiated from monitoring results. Shell monitoring is conducted using a TLV instrument which is a catalytic combustion analyzer [photograph 6]. VOC readings are recorded on inventory lists for each operating unit and forwarded to Environmental Conservation. Repair lists, follow-up monitoring lists, monthly summary reports, and quarterly summary reports are developed from this information.

Monitoring Results

NEIC conducted an audit of the Shell LDAR program November 15 through 19, 1993. The audit was divided into two parts, monitoring of VOC components by NEIC personnel, and evaluating the refinery's monitoring procedures. NEIC personnel inspected components in benzene service in five process units and VOC components in two NSPS units.

NEIC monitored 2,008 valves and identified 108 leaking (10,000 ppm leak definition used for valves and connectors, and 1,000 ppm used for pumps and compressors) [Table 7]. NEIC monitoring was conducted by a three-person team using Century System OVAs, Model OVA-108. Shell personnel present during the monitoring did not attempt to verify leaking components. NEIC provided Shell with a list of leaking components at the end of each day.

Shell did not meet the 2% allowable percentage of valves leaking under the alternative standard for valves in volatile hazardous air pollutants (VHAPs) service. Process units monitored by NEIC were operating under the

Table 7

VOC VALVE MONITORING RESULTS
Shell Oil Refinery
Roxana, Illinois

Process Unit		NEIC Monitoring			Shell Reported % Leaking*
Number/Name	Valves Benzene/NSPS Service	Components Monitored	Leaking Valves Identified	Percent Leaking	
Benzene Extraction	1,166	425	33	7.8	0.8
Catalytic Reformer - 1	520	345	21	6.1	0.8
Catalytic Reformer - 3	355	288	21	7.3	1.5
Dispatching	361	230	9	3.9	0
Utilities	206	135	0	0	0
Catalytic Dewaxing	438	292	21	7.2	0.4
Deasphalting	867	293	3	1.0	0.2
Plant Wide Totals	---	2,008	108	5.4	---

* *Based on most recent monitoring period for each process unit*

alternative standards for valves allowing a 2.0% valve leak rate for each unit. Shell monitors valves in benzene service and valves in NSPS units annually as outlined in 40 CFR § 61.112 and 40 CFR § 60.483. NEIC identified four units in benzene NESHAP service with leak rates greater than 2% including: benzene extraction unit, catalytic reformer-1, catalytic reformer-2, and dispatching. NEIC also determined a leak rate greater than 2% at the catalytic dewaxing unit, an NSPS unit [Table 8].

The NEIC monitoring inspection focused on valves in NESHAP and NSPS service. Miscellaneous connectors* attached to valves were included in the monitoring. The majority of the connectors inspected included pressure gauge connections and secondary plugs placed in valve openings. NEIC monitored less than 100 connectors. Connectors are not required to be uniquely identified or routinely monitored.

The percentage of leaking components found during the NEIC monitoring program is greater than that found by the Shell monitoring. Table 7 presents a summary of the NEIC and Shell monitoring results for seven process units. Possible reasons for the differences in leak rates include:

- Shell uses a TLV instrument for monitoring components. TLVs have a slower response time than the OVA. OVAs response is less than 10 seconds to the VOC being measured; however the TLV response time is approximately 30 seconds.

- The monitoring procedures used by NEIC were more deliberate than those used by refinery personnel.

* *Flanged, screwed, or other joined fittings used to connect two pipe lines or pipe line and piece of process equipment.*

Table 8

ALTERNATIVE STANDARD VOC VALVE MONITORING RESULTS
Shell Oil Refinery
Roxana, Illinois

Process Unit		NEIC Monitoring			
Number/Name	Valves	Service	Alternative Standard 2% Total Valves	Leaking Valves Identified	Exceeds 2% Limit
Benzene Extraction	1,166	Benzene	24	33	Yes
Catalytic Reformer - 1	520	Benzene	11	21	Yes
Catalytic Reformer - 3	355	Benzene	7	21	Yes
Dispatching	361	Benzene	8	9	Yes
Utilities	206	Benzene	4	0	No
Catalytic Dewaxing	438	NSPS*	9	21	Yes
Deasphalting	867	NSPS	18	3	No

* *Unit is regulated by New Source Performance Standards*

Missing, misaligned, or loosely fitting plugs in the end of the valves were a source of fugitive VOC emissions. NSPS and Benzene NESHAP regulations require each open-ended valve or line to be equipped with a cap, blind flange, plug or second valve; however, non-NSPS processes do not need to meet this requirement. No leaking plugs were identified in NSPS processes of the refinery. Two missing plugs were identified in the benzene extraction unit (BEU), valve numbers A-000256 and A-000258. One open end was found at catalytic reformer (CR) -1, a sample point on P-69020 near valve number B-000348.

Jurgason valves on reactor level gauges are a source of fugitive VOC emissions. Shell is inconsistent in monitoring these valves. Jurgason valves are included in the monitoring program at some process units and not at others. Additional valves on the level gauges are tagged and monitored. NEIC identified several valves that were not uniquely identified and were leaking, including two valves at the catalytic dewaxing unit on the level gauge for vessel 4728 and two valves on vessel 1803 at the deasphalting unit.

Motorized valves (MOV) are a source of fugitive VOC emissions. Ten MOVs on the CR-1 reactors, and eight MOVs on the CR-3 reactors were found leaking. At least one MOV on the top of Reactor D at CR-1 was a source of significant VOCs. The OVA background reading on Reactor D was in excess of 1,000 ppm and hydrocarbons could be seen leaking from the MOV.

During the NEIC inspection, deficiencies were noted in the Shell tagging system for VOC components, as summarized below:

- Three valves near tag A-000239 in the BEU were not tagged and were leaking. Numerous sampling valves throughout the refinery were not tagged.

- Duplicate identification numbers (a similar tag number was attached to two different components) were observed on components in the BEU. Two duplicate tag numbers, C-000231 and B-000011, were used.

- Identification tags were missing from less than 50 components. The identification number for most of these untagged components was determined by assuming sequential component numbering and using the component log. Missing identification tag numbers are identified by the unit monitoring personnel and replaced during the next monitoring period.

Shell instrument calibration procedures do not meet the requirements outlined in Method 21. The TLV monitor is calibrated using a zero span gas and 3,000 ppm hexane instead of the 10,000 ppm leak standard value required in Method 21. Shell correspondence to Region 5 on April 23, 1990 requested the use of 3,000 ppm hexane for the calibration procedures [Appendix N]. Shell provided the region with data indicating response of the TLV is adequate using 3,000 ppm hexane for calibration. Region 5 responded on May 15, 1990 allowing Shell to use an alternate calibration gas of 3,000 ppm [Appendix O]. Using a calibration gas lower than the leak standard may affect the accuracy of the instrument for readings greater than 3,000 ppm.

Records Review

Permits

The refinery air permits were reviewed. Several issues were identified which may need to be addressed in order to avoid potential misunderstandings between the facility and the regulatory agencies.

Permit No. 72110620 (WRR-6) specifies different H_2S concentration limits for the fuel gas used in the vacuum flasher process heaters. An H_2S limit of 0.1 gr/dscf is identified in permit condition 1b when discussing NSPS requirements for heaters VF-1-N and VF-1-S. Permit condition 6b identifies an H_2S limit of 39 gr/100 dscf for <u>all</u> process heaters in the vacuum flasher unit. The 39 gr/100 dscf is intended for the non-NSPS heaters. Clarification to the permit should be considered to eliminate possible confusion in the conflicting requirements of conditions 1b and 6b. Currently, the refinery is using the 0.1 gr/dscf limit for the two NSPS heaters and the 39 gr/100 dscf limit for the three non-NSPS heaters.

The permits for CCU-1 and CCU-2 (Permit Nos. 72110621 and 721106216) allow ammonia injection for conditioning the ESP until fully energized. However, discussions with refinery personnel indicated that ammonia is not injected during start-up, but is continuously injected to extend the maintenance cycle of the ESP. The injection of ammonia was not addressed in copies of the original permit applications provided by the refinery. Approximately 170,000 pounds of ammonia were emitted from the CCUs during 1992.*

Quarterly Reports

Shell is required to submit quarterly SO_2 emissions, NSPS emissions, CCU opacity, and boilers 15, 16, and 18 opacity reports. Several issues were identified during the review of these reports.

Quarterly SO_2 reports from the fourth quarter 1990 through the third quarter 1993 were reviewed. The reports are generally submitted within 30

* *Information obtained from 1992 Form R submittal.*

days of the end of the quarter; however, the first quarter report for 1993 was submitted on May 3, 1993. The reports list the total monthly SO_2 emissions and the highest and second highest daily emission rates, as required by the permits.

Compliance with the individual SOG SO_2 limits cannot be determined from the information provided on the quarterly SO_2 reports. The reports list only daily and monthly totals. Compliance with the individual SOG SO_2 limits are based on a 3-hour block average [IAC 214.382(d)]. Shell maintains records for hourly and 3-hour block average SO_2 emissions, as required in the permits, but this information is not provided or required on the monthly reports.

The maximum total daily SO_2 emission on the reviewed reports was 95 tons per day compared to the computed permit limit of approximately 117 tons per day. Refinery personnel indicated that there had been no SO_2 emissions in excess of the individual SOG limits. NEIC personnel conducted spot checks of the individual hourly SOG SO_2 limits and no excess emissions were identified.

The combined quarterly NSPS H_2S reports for the Vacuum Flasher, boiler 18, Acetone, and Catalytic Dewaxing units were reviewed. During the reviewed period, from the fourth quarter 1990 through the third quarter 1993, the acetone and catalytic dewaxing units were out of service. Reportedly only natural gas was burned in each NSPS unit and there were no excess emissions of H_2S.

Quarterly NSPS opacity reports for boiler No. 17 from the fourth quarter 1992 through the third quarter 1993 were reviewed. The boiler was operated on RFP during portions of the second and third quarters of 1993. The second and third quarter NSPS reports state "boiler 17 was operated on pitch (non-

fossil fuel) and not covered by NSPS during most of this reporting period" [Appendix P]. The time periods when the boiler is burning fossil fuel are the only periods included on the quarterly NSPS reports. The opacity results for boiler 17 when burning RFP are included on the boilers 15, 16, and 18 quarterly opacity reports.

Boiler 17 quarterly NSPS opacity reports document excess opacity emissions. The 20% opacity limit was exceeded during three of the four quarters, when RFG was burned, as shown below:

Reporting Period	Opacity greater than 20% (minutes)	Time operated on fossil fuel (minutes)
3rd quarter 93	0	11,520
2nd quarter 93	6	93,600
1st quarter 93	18	129,480
4th quarter 92	36	129,480

The CCU-1 and CCU-2 opacity reports for the first quarter 1991 through third quarter 1993 were reviewed. The excess opacity readings, greater than 30%, for these units during this period are presented in Appendix Q. The permits for CCU-1 and CCU-2 require that the opacity be averaged over a 6-minute period. The 30% opacity limit averaged over 6-minute periods has been exceeded 183 times from July 1992 through October 1993. Shell has attributed a majority of the excess emissions to either power failure, blower tripped, soot blowing, or high hopper levels.

The IAC allows the 30% opacity standard to be exceeded during startup, malfunction, and break-down. Opacity readings between 30 and 60% are allowed for a period or periods aggregating 8 minutes in any 60-minute period provided that no more than three such excess emissions occur in any 24-hour period. No exception is allowed for opacity readings greater than 60%.

The combined quarterly opacity reports for boilers No. 15, 16, and 18 for the fourth quarter 1990 through third quarter 1993 were reviewed. Included in these reports are the opacity data for boiler 17 when RFP is burned.*

There have been five boiler 15 excess opacity emissions from the first quarter 1991 through the third quarter 1993, as summarized below:

Date	Time	Average % Opacity	Explanation
9/16/93	2227-2233	58	Fuel system upset
3/09/93	1356-1402	35	O_2 analyzer malfunction
11/2093	1944-1950	31	O_2 analyzer malfunction
11/27/93	2008-2014	58	O_2 analyzer malfunction
11/27/93	2014-2020	39	O_2 analyzer malfunction

There have been two Boiler 16 excess opacity emissions from the first quarter 1991 through the third quarter 1993, as summarized below:

Date	Time	Average % Opacity	Explanation
9/01/93	1345-1531	33	Fuel switch
8/23/93	1903-1909	32	Steam Upset

Excess opacity emissions were reported for boiler 17 only during the third quarter 1993. Shell reported 30 6-minute average periods when the opacity exceeded 30% [Appendix R]. Shell considers the opacity limit for this unit to be 30% because a nonfossil fuel is used (see discussion on page 14).

* *Shell considers the boiler to be non-NSPS when RFP is burned.*

The opacity limits for boiler 17 should be 20% because the Wood River RFP has not been designated a "non-fossil fuel," thus subjecting the unit to NSPS opacity limit of 20%. NSPS regulations allow opacity reading to exceed 20% for one 6-minute period per hour of not more than 27% opacity. Thirty 6-minute average opacity readings exceeded 27%. Each excess opacity reading was attributed to soot blowing.

The IAC allows the 20% opacity standard to be exceeded during startup, malfunction, and break-down. Opacity readings between 20 and 40% are allowed for a period or periods aggregating 3 minutes in any 60-minute period, provided that no more than three such excess emissions occur in any 24-hour period. No exception is allowed for opacity readings greater than 40%. Using the opacity exceptions and the information presented in the third quarter 1993 report, the opacity exceeded the 40% limit for at least one 3-minute period.

Excess Emissions

The Shell "IEPA Malfunction Reports" were reviewed from January 1991 through October 26, 1993. These reports identify numerous excess emissions from the sulfur recovery units and exceedances of the 39 gr H_2S/100 dscf limit for the RFG.

The 1,000 ppm SO_2 limit for the sulfur recovery unit emissions was exceeded on 28 occasions from February 1991 through October 1993 [Table 9]. Compliance with the 1,000 ppm SO_2 standard is based on a 3-hour average time period. Generally, the reported excess SO_2 emissions were for one 3-hour period; however, there was one excess emission in which 38 consecutive 3-hour periods were exceeded. During the excess emissions, the quantity of SO_2 released ranged from 25 pounds to 1,576 long tons.

Table 9
SO_2 EXCESS EMISSION SUMMARY
Shell Oil Refinery
Roxana, Illinois

Date	Estimate of Excessive Emission	Duration
10/19/93	0.236 long tons	One 3-hour average period
8/30/93	0.96 long tons	Two 3-hour average periods
7/7/93	7.0 long tons	Two 3-hour average periods
7/6/93	0.4 long tons	One 3-hour average period
3/2/93	0.58 long tons	One 3-hour average period
2/7/93	0.115 long tons	One 3-hour average period
12/16/92	15.8 long tons	Four 3-hour average periods
12/5/92	12.1 long tons	Three 3-hour average periods
11/17/92	3.2 long tons	One 3-hour average period
11/7/92	98 pounds	One 3-hour average period
10/5/92	9.3 long tons	Two 3-hour average periods
9/17/92 - 9/18/92	5.8 long tons	Nine 3-hour average periods
9/10/92 - 9/11/92	10.8 long tons	Four 3-hour average periods
8/24/92 - 8/26/92	377 pounds	Three 3-hour average periods
6/5/92	16.7 long tons	Four 3-hour average periods
4/22/92	1,576 long tons	Conducted scheduled maintenance 4/22/92 - 6/1/92
3/16/92	25 pounds	One 3-hour average period
11/3/91	8.8 long tons	Two 3-hour average periods
7/2/91	128 pounds	One 3-hour average period
6/28/91	32 pounds	One 3-hour average period
6/18/91	10.7 long tons	Four 3-hour average periods
7/16/91	140 pounds	One 3-hour average period
4/30/91	0.2 long tons	Three 3-hour average periods
3/27/91	50 pounds	One 3-hour average period
6/1/91	4,800 pounds	One 3-hour average period
5/31/91 - 5/30/91	29 pounds	One 3-hour average period
3/7/91 - 3/10/91	151 long tons	Thirty-one 3-hour average periods
3/4/91	31 long tons	seven 3-hour average periods
2/9/91	2.5 long tons	Four 3-hour average period
2/4/91	0.1 long tons	One 3-hour average period

The permit allows excess emissions provided that IEPA is notified immediately. Shell does not maintain records to document when the IEPA was initially notified of an excess emission. The Shell "IEPA Malfunction Reports" are typically submitted within 1 week of the actual excess emission.

The 39 gr H_2S/100 dscf limit for the RFG limit was exceeded on 22 occasions from January 1991 through October 1993 [Appendix S]. Provisions of the affected process units allow the IAC limit of 39 gr H_2S/100 dscf limit to be exceeded, provided the SOG limits are not exceeded.

SUMMARY OF FINDINGS

AREAS OF NONCOMPLIANCE

Shell air contaminant emissions are regulated by the Illinois air regulations and 35 operating permits. In addition, sources are subject to the U.S. EPA New Source Performance Standards (NSPS, 40 CFR Part 60) and the National Emission Standards for Hazardous Air Pollutants (NESHAP, 40 CFR Part 61). The following areas of noncompliance of these regulations were identified during the NEIC investigation.

40 CFR § 60.40 (c)	When fired with refinery fuel pitch, boiler No. 17 is not operated in accordance with NSPS requirements. Inappropriate monitoring and recordkeeping are maintained.
35 IAC Section 215.144(d)	On five occasions, the number of excessive organic releases from safety relief valves has exceeded three in a 12-month period.
40 CFR § 61.243-1, as referenced by 40 CFR § 61.112 (b)	Shell exceeded the 2% allowable for valves leaking under the alternative monitoring standard. NEIC identified four units in Benzene NESHAP service with leak rates greater than 2% including: - Benzene Extraction Unit - Catalytic Reformer-1 - Catalytic Reformer-3 - Dispatching
40 CFR § 60.483-1, as referenced by 40 CFR § 60.592 (b)	Shell exceeded the 2% allowable for valves leaking under the NSPS alternative monitoring standard. NEIC determined a leak rate greater than 2% at the Catalytic Dewaxing Unit.

40 CFR § 61.242-6	Plugs, caps, blind flanges, or secondary valves were missing from two benzene NESHAP unit valves with tag numbers A-000256 and A-000258.
40 CFR § 61.242-1 (d)	Five valves in the benzene extraction unit were not marked in a manner to distinguish them from other equipment. Three valves near tag number A-000239 were not tagged, and two duplicate tag numbers (C-000231 and B-000011) were identified.
35 IAC Section 212.123	Excess emission reports from January 1, 1991 through October 1993 were reviewed and the 30% opacity limits for CCU-1 and CCU-2 were exceeded. CCU-1 opacity was between 30 and 60% during 19 6-minute periods and exceeded the 60% limit during 4 6-minute periods. CCU-2 opacity was between 30 and 60% during 30 6-minute periods and exceeded 60% during 55 6-minute periods.
40 CFR § 60.42 (a)(2)	Boiler No. 17 opacity exceeded the maximum allowable limit of 27%. This limit was exceeded on 30 six-minute periods, during the third quarter of 1993.

AREAS OF CONCERN*

- There is no emission monitoring of the CCU bypass stacks. When the CO boiler and/or ESP is down for maintenance or during an upset condition, the exhaust gases are vented directly to the auxiliary stack. Significant emissions are released through these stacks during bypass events.

* *Areas of concern are inspection observations of potential problems that could result in noncompliance with permit or regulatory requirements, or are areas associated with pollution prevention issues.*

- The CCU stack tests may not accurately reflect the emission rates from the CCU-1 and CCU-2. Soot blowing activities were curtailed during the stack tests.

- The H_2S fuel content for vacuum flasher heaters 1 and 2, the catalytic dewaxer heater, and boiler 18 (NSPS units) is not monitored when natural gas is burned. These units are connected to both the RFG and natural gas supply systems. The RFG supply line has been blocked (not removed) and only natural gas is exclusively routed to the heaters. RFG H_2S content is continuously monitored; however, the natural gas H_2S content is not monitored. Shell should be required to clearly report when fuel types are changed.

- Remediation groundwater used in the refinery is contaminated with benzene and is a significant source of benzene emissions. The benzene in the extracted groundwater does not need to be included in the TAB; however, the water streams containing more than 10 ppm benzene must be controlled in accordance with Subpart FF. Benzene control measures for the well water streams containing greater than 10 ppm benzene were not included in the Application for Waiver of Compliance.

- The VOC component leak rate determined by NEIC was greater than the leak rate reported by Shell for six units inspected. The NEIC and Shell leak rates for monitored units are summarized below:

Process Unit	NEIC Leak Rate %	Shell Leak Rate %
Benzene Extraction	7.8	0.8
Catalytic Reformer-1	6.1	0.8
Catalytic Reformer-3	7.3	1.5
Dispatching	3.9	0.0
Catalytic Dewaxing	7.2	0.4
Deasphalting	1.0	0.2

- Missing or loosely fitting plugs at the end of open-ended valves were the source of several VOC leaks. Secondary closure devices such as caps, blind flanges, plugs, or second valves are only required for NSPS and NESHAP regulated portions of the facility. Most refinery portions are not covered by these requirements.

- Jurgason valves on reactor level gauges are a source of fugitive VOC emissions. Shell is inconsistent in monitoring these valves. Jurgason valves are included in the monitoring program at some process units and not at others. Other valves on the level gauges are tagged and monitored. NEIC identified several Jurgason valves that were not uniquely identified and were leaking, including two valves at the catalytic dewaxing unit on the level gauge for vessel 4728 and two valves on vessel 1803 at the deasphalting unit.

- Motorized valves (MOVs) are a significant source of fugitive VOC emissions. Ten MOVs on the CR-1 reactors, and eight MOVs on the CR-3 reactors were found leaking. At least one MOV on the top of Reactor D at CR-1 was a source of significant VOCs. Hydrocarbons could be seen leaking from the Reactor D MOV and the OVA <u>background</u> reading was in excess of 1,000 ppm.

- Shell instrument calibration procedures do not meet the requirements outlined in Method 21. The TLV monitor is calibrated using a zero span gas and 3,000 ppm hexane instead of the 10,000 ppm leak standard value required in Method 21. Shell correspondence to Region 5 on April 23, 1990 requested the use of 3,000 ppm hexane for the calibration procedures. Shell provided the Region with data indicating response of the TLV is adequate using 3,000 ppm hexane for calibration. Region 5 responded on May 15, 1990 allowing Shell to use an alternate calibration gas of 3,000 ppm. Using a calibration gas lower than the leak standard may affect the accuracy of the instrument for readings greater than 3,000 ppm.

- The refinery will need to improve the VOC program in order to comply with the 2% alternative standard requirements. In order to comply with the requirements, the refinery may need to replace some of the older valves with newer technology.

- Inconsistences exist within permit No. 72110620 (WRR-6) in limiting H_2S concentration in the fuel gas used in the vacuum flasher process heaters. Condition 1b specifies an H_2S limit of 0.1 gr/dscf and condition 6b identifies a 39 gr/100 dscf limit. Clarification of the permit should be considered to eliminate possible confusion in the conflicting requirements of conditions 1b and 6b.

- Emission of approximately 170,000 pounds of ammonia from CCU-1 and CCU-2 is unregulated. The permits for the CCU-1 and CCU-2 allow ammonia injection for conditioning during start-up of the electrostatic precipitator (ESP). Discussions with refinery personnel indicated that ammonia is injected periodically to extend the maintenance cycle of the ESP, not during start-up.

- Compliance with the individual SOG SO_2 limits cannot be determined from the information provided on the Shell quarterly SO_2 reports. The reports list only daily totals and compliance is based on a 3-hour block average. Shell maintains records for hourly and 3-hour block average SO_2 limits, as required in the permits, but this information is not provided or required on the quarterly reports.

- The 1,000 parts per million (ppm) SO_2 limit for the sulfur recovery unit emissions was exceeded on 28 occasions. Several of these excess emissions, due to upsets, malfunction, or breakdowns, resulted in releases of tons of SO_2. Operating and maintenance practices should be reviewed to minimize these excess emissions.

- The 39 H_2S gr/100 dscf Illinois Administrative Code (IAC) limit for the refinery fuel gas (RFG) limit was exceeded on 22 occasions from January 1991 through October 1993. Permit provisions of the affected process units allow the IAC limit of 39 H_2S gr/100 dscf limit to be exceeded.

CLEAN WATER ACT
NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM

MULTI-MEDIA COMPLIANCE INVESTIGATION

SHELL OIL COMPANY
Wood River Manufacturing Complex
Roxana, Illinois

Facility Address

Shell Oil Company
Wood River Manufacturing Complex
Highway 111
Roxana, Illinois 62084
(618) 255-2478

Investigation Dates

October 25 through November 9, 1993

Lead Investigator

Daren Vanlerberghe, Environmental Engineer
NEIC

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MEDIA REPORT

At the request of EPA Region 5, NEIC conducted a multi-media compliance investigation of the Shell Oil Company - Wood River Manufacturing Complex (Shell), a petroleum refinery located in Roxana, Illinois. This report, one of a series that addresses investigation findings, discusses Clean Water Act (CWA) issues and compliance with the applicable regulatory requirements.

REGULATORY SUMMARY

Shell is regulated by a National Pollutant Discharge Elimination System (NPDES) permit because they directly discharge treated wastewater to the Mississippi River. Shell also discharges stormwater to Grassy Lake, a tributary to Cahokia Canal. Shell operates a petroleum refinery to produce gasolines, fuel oil, asphaltic products, and lube products (Standard Industrial Code 2911). Shell is, therefore, subject to the following CWA regulation: Effluent Guidelines and Standards for the Petroleum Refining Point Source Category [40 CFR Part 419].

EPA Region 5 delegated the NPDES program to the Illinois Environmental Protection Agency (IEPA). NPDES Permit Number IL0000205 [Appendix A] was reissued by IEPA to Shell on July 5, 1993. The permit became effective on August 5, 1993 and expires on June 15, 1998. The permit was based on the above referenced Effluent Guidelines and Illinois water quality standards. The previous NPDES permit [Appendix B] was issued on June 9, 1988 and expired on the effective date of the current permit.

The permit authorizes the discharge of wastewater through 10 outfalls [Figure 1]. Refinery process wastewater, sanitary wastewater, stormwater, and cooling tower blowdown from Cardox, an adjacent facility, is treated and

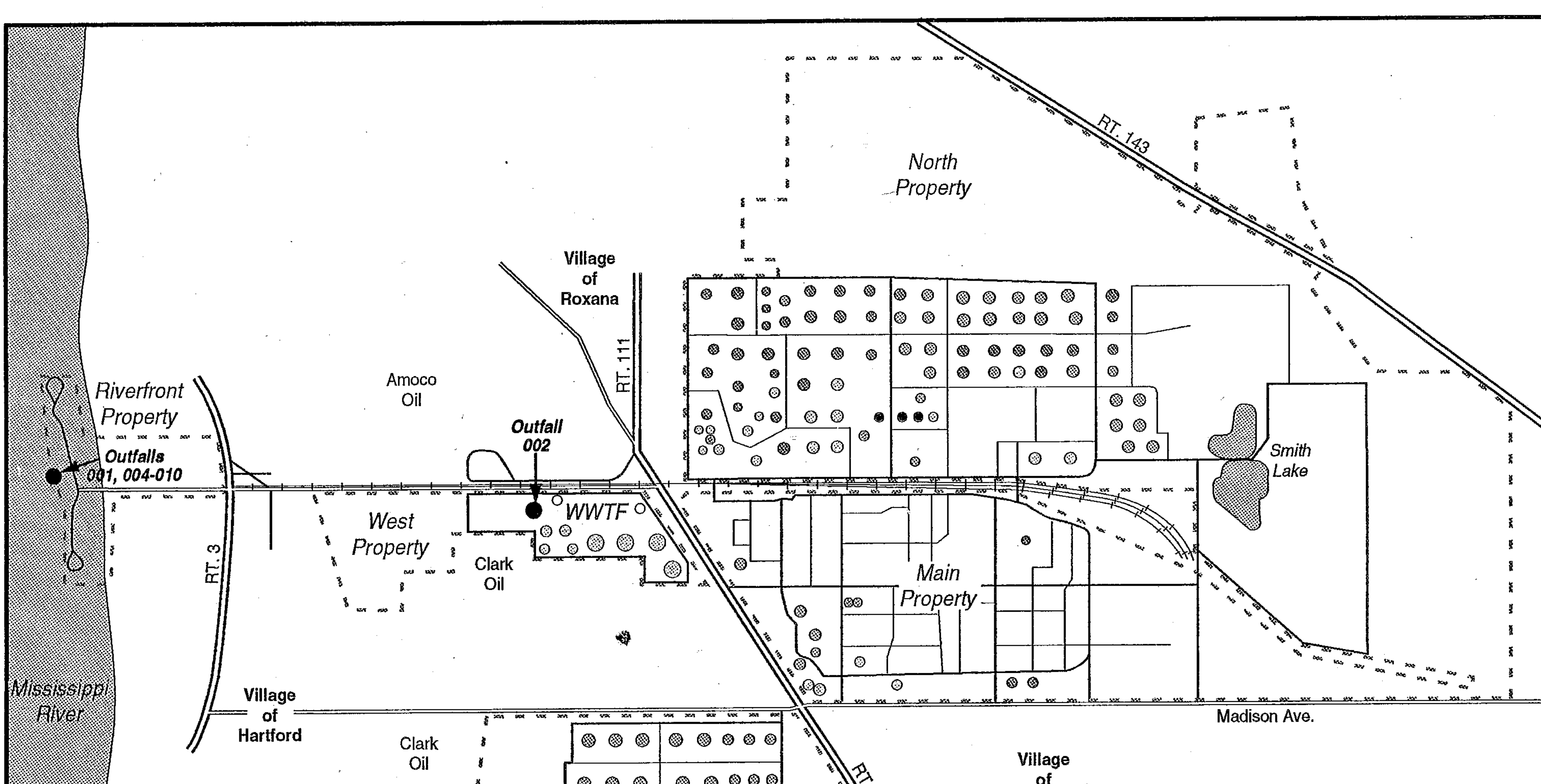

Figure 1
NPDES OUTFALL LOCATIONS
Shell Oil Company
Wood River Manufacturing Complex
Roxana, Illinois

discharged to the Mississippi River through outfalls 001 and 002. Treated effluent from the Village of Roxana's Sewage Treatment Plant is discharged through Shell's polishing lagoons to outfall 001. Outfall 002 is an alternate monitoring location authorized by the permit when outfall 001 "is impossible to monitor, due to flood conditions." Outfall 002 is the secondary clarifier effluent located at Shell's wastewater treatment plant (WWTP). Excessive stormwater runoff from the main property, north property, and southwest tank farm area is discharged through outfall 003 to Grassy Lake, a tributary to Cahokia Canal which flows to the Mississippi River. First flush stormwater is collected and pumped to the process sewer for treatment at the WWTP. Stormwater runoff from Shell's dock area is discharged untreated to the Mississippi River through outfalls 004 through 010.

Permit limitations for outfalls 001 and 002 were based upon the federal effluent guidelines, Illinois Pollution Control Board regulations, and state water quality standards. Table 1 shows the permit limitations and monitoring frequencies for outfalls 001 and 002. Permit limitations for outfall 003 are established for pH and oil and grease. There are no permit limitations for outfalls 004 through 010.

The specific rationale for the NPDES permit limitations are contained in the IEPA Fact Sheet and Engineer Review Notes [Appendix C]. IEPA classified Shell under 40 CFR Part 419, Subpart D - Lube Subcategory, for determining production based effluent limitations. The production basis for the permit limitations was 270,000 barrels of crude oil per stream day.

ON-SITE INSPECTION SUMMARY

Credentials were presented to Joseph N. Brewster, Environmental Conservation Manager, Shell. Following a general discussion of plant

Table 1

NPDES PERMIT LIMITATIONS FOR OUTFALLS 001 AND 002
Shell Oil Refinery
Roxana, Illinois

Parameter	Load Limits (pounds/day)		Concentration Limits (mg/L)		Monitoring Frequency
	30 Day Average	Daily Maximum	30 Day Average	Daily Maximum	
pH	The pH shall be within the range of 6.0 to 9.0.				2/week
BOD_5	1,318	4,570	20	40	2/week
TSS	1,647	5,451	25	50	2/week
TDS	-*	799,819	-	5,156	1/month
COD	27,524	53,314	-	-	2/week
Oil & grease	988	2,363	15	30	1/week
Phenols	19.8	27.92	-	0.18	2/week
Ammonia as N April-October November-March	788 1,501	3,258 3,458	10.5 20	21 40	2/week 2/week
Sulfides	22	49	-	-	2/week
Total chromium	24	69	0.36	2.0	2/week
Hexavalent chromium	1.98	4.42	0.04	0.05	2/week
Total cyanide	7.51	31	0.1	0.2	1/month
Sulfate	-	359,888	-	2,320	1/month
Chlorides	-	241,993	-	1,560	1/month

* *- means no established limits*

processes, including byproduct/waste generation and handling, a plant tour was conducted. The following facility areas were inspected: the water supply, various wastewater generation points, wastewater treatment, the stormwater outfalls, and monitoring procedures and locations. Records/documents affiliated with regulated activities were also reviewed. Photographs referenced in this report are provided in Appendix D. Exit conferences between regulatory and refinery personnel [Appendix E] were conducted to discuss preliminary inspection findings. NEIC personnel stressed that final determinations will be made in conjunction with regional and state personnel.

Facility Inspection/Discussions

Water Supply and Wastewater Generation

Shell uses on-site well water for all processes. Cooling water and boiler feed water are treated in separate areas before use. All potable water used on-site is from the Village of Roxana municipal water supply. Figure 2 shows a diagram of water and wastewater flows at Shell based on information provided in their 1992 NPDES permit application.

From October 1992 to September 1993, Shell discharged an average of 6.5 million gallons per day (mgd) to the Mississippi River through outfalls 001 and 002. There is no requirement to monitor flow for the stormwater discharged through outfalls 003 through 010.

Wastewater Treatment

Shell's WWTP consists of screening, neutralization, oil/water separation, dissolved air flotation (DAF) thickening, equalization, biological treatment, clarification, and polishing. Figure 3 is a block flow diagram of Shell's WWTP.

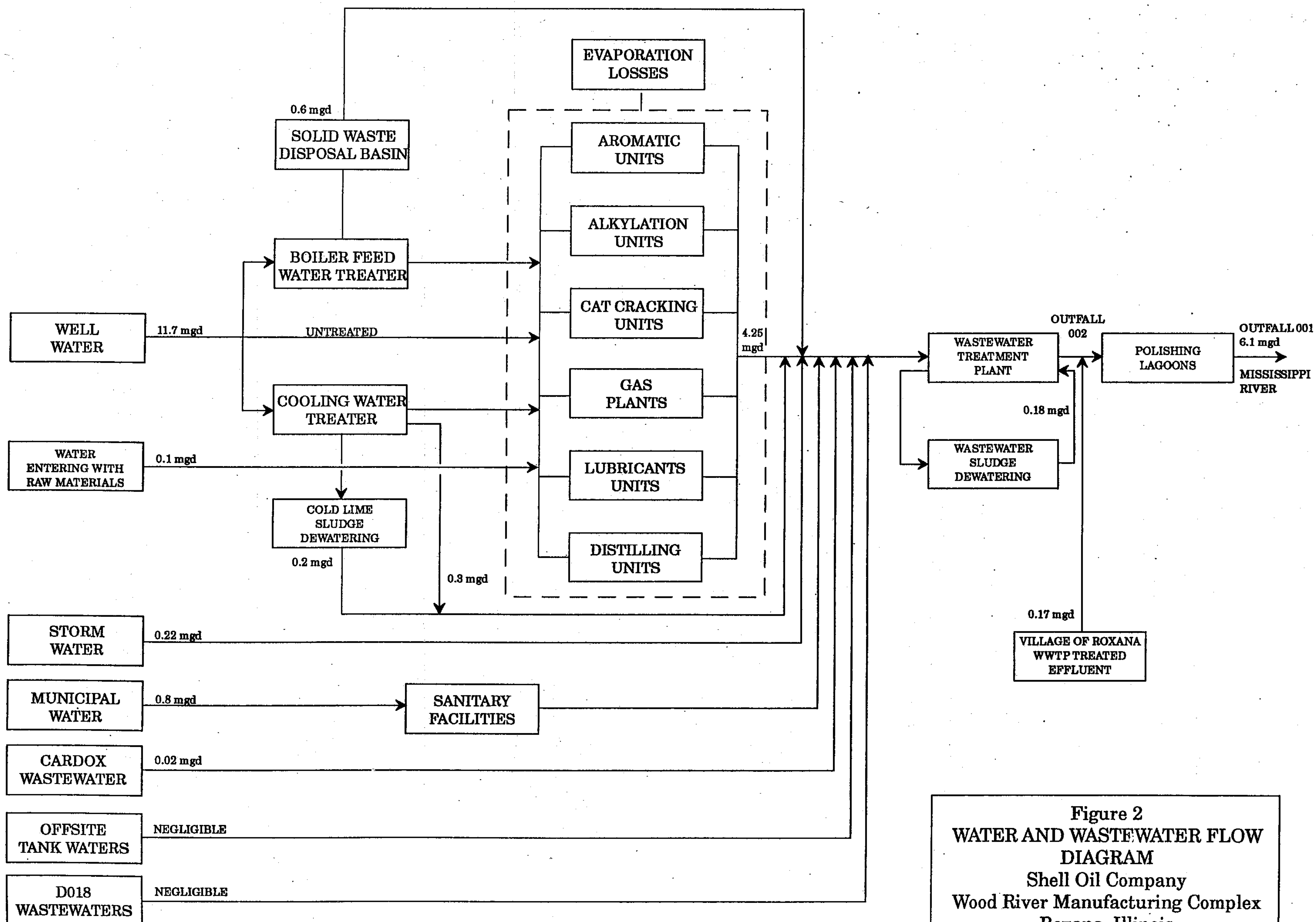

Figure 2
WATER AND WASTEWATER FLOW DIAGRAM
Shell Oil Company
Wood River Manufacturing Complex
Roxana, Illinois

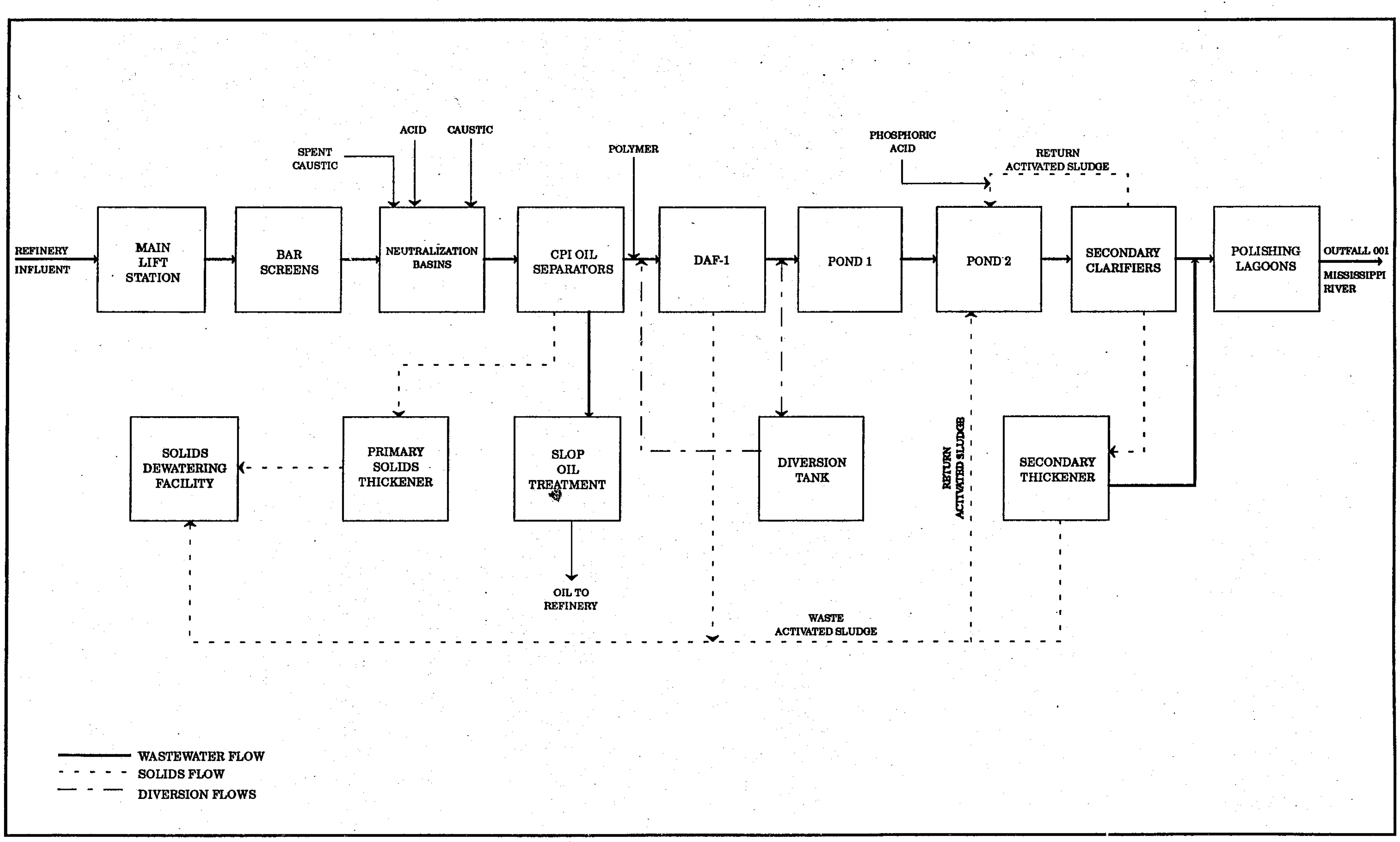

Figure 3
WASTEWATER TREATMENT PLANT BLOCK FLOW DIAGRAM
Shell Oil Company
Wood River Manufacturing Complex
Roxana, Illinois

A $55 million upgrade of the WWTP was completed in 1990. The upgrade included a new lift station, addition of a diversion tank, secondary clarification, and miscellaneous internal renovations. Shell is currently in the process of another upgrade which should be completed in 1994. This upgrade will include the addition of a DAF unit and modification of biological treatment.

Refinery wastewater enters the WWTP at the lift station basin, where it is lifted by three Archimedes screw pumps for subsequent treatment. The screw pumps are rated at 6,000 gallons per minute (gpm) capacity each. One pump is capable of handling the normal influent wastewater flow to the lift station. However, two pumps are typically operated with the third pump set to start automatically during extremely high flow conditions. The lift station basin is covered and vented to a volatile organic compounds (VOC) emission recovery system. The pumps and drive shafts are sealed to prevent fugitive VOC emissions.

The lifted wastewater discharges into a basin equipped with two bar screens to remove large debris. Each bar screen has a rake to remove debris collected on the screens. The removed material is raked into bins and shipped as hazardous waste off-site for incineration. The rakes run automatically based on water level differential across the screens. The bar screen basin is covered and vented to the VOC emission recovery system.

Wastewater flows by gravity from the bar screens into a two-stage neutralization system. The neutralization system consists of two 47,000-gallon mixing basins run in series, each with independent acid and caustic feed systems. The targeted pH range of the system is 7.0 to 9.5. Spent caustic from refinery processes is collected in a tank at the WWTP where it can be fed into the neutralization system. This reduces the use of fresh caustic in the system. Spent caustic was originally being fed into the main lift station.

However, this caused calcium precipitation in the screw pumps, so the practice was changed.

Neutralization effluent flows into the corrugated plate interceptor (CPI) separation system. The CPI system operates in parallel and consists of two trains with four CPI separators to each train. Each separator has five fiberglass reinforced plastic (FRP) plates which induce oil to the top and solids to the bottom of the separator. CPI effluent flows by gravity to the dissolved air flotation system (DAF-1). Floating oil from all eight separators is sent to the slop oil treatment system for further oil/water separation and to break emulsions. The slop oil system consists of one CPI oil tank and three heated slop oil tanks. Floating oil is collected in the CPI oil tank and skimmed into one of the slop oil tanks. The oil enters either tank D-52 or D-53, alternating on a daily basis. While one tank is filling and being heated to 175 °F, water and oil are withdrawn from the other tank. The remaining emulsion layer is sent to the third slop oil tank (D-54) for heat and chemical emulsion breaking. All recovered oil in the slop oil system is returned to the refinery for reprocessing. The water that is separated in the system is returned to the lift station. Any emulsion layers that cannot be broken up, referred to as the "rag layer," are pumped out and disposed of as hazardous waste (EPA hazardous waste number K049). In 1993, no "rag layer" material was generated.

Solids which settle in the CPI separators are collected in sludge hoppers and pumped to a primary solids thickener. Polymer may be added to the sludge for conditioning. Thickened sludge is pumped to the Heritage solids dewatering facility.

CPI effluent flows by gravity to the DAF-1 system which further reduces the suspended oil and solids prior to biological treatment. Polymer is added to DAF-1 influent to improve coagulation of oil and solid particles. Floated material is collected on the surface and skimmed with a raking mechanism. Heavier material settles to the bottom of the unit and raked into a solids sump. The floated and settled material is sent to the solids dewatering facility. Clarified wastewater passes under a baffle and flows by gravity to Pond 1. Shell is in the process of constructing an additional DAF unit. This unit should be on-line in early spring 1994.

CPI effluent to DAF-1 can be diverted to Diversion Tank (A-149) during excessive flows or when the wastewater contains high concentrations of total organic carbon (TOC). The tank has a capacity of about 7,200,000 gallons, which is designed for a 1-day detention time. Wastewater in the tank is released at a controlled rate to either Pond 1 or DAF-1. The tank, equipped with agitators to keep material suspended, is used to maintain a uniform flow back to the system.

Pond 1 is used to equalize flows and organic loads prior to biological treatment. The pond is a 14-feet-deep earthen basin with a capacity of 3,000,000 gallons. Pond 1 is equipped with a floating skimmer to collect surface oil and transfer it back to the slop oil system. Pond 1 effluent flows to the Pond 2 aeration basin. Pond 1 effluent originally flowed to a trickling filter. The trickling filter was removed from service in April 1993. Pond 1 will be replaced by a tank when the current upgrade to the WWTP is completed.

Pond 2 provides biological treatment through the activated sludge process. The earthen pond has a capacity of approximately 4.2 million gallons. The pond is equipped with 15 surface aerators with a combined total aeration capacity of 525 horsepower. At the time of the NEIC inspection, 10 aerators were operating. Because the aerators provide some cooling to the pond, a WWTP operator stated it is common practice to operate less aerators in order to keep the temperature of the pond at or above 70 °F for nitrification

purposes. Shell personnel were not aware if this causes solids deposition near the down aerators, and the pond has not been cleaned out in recent memory.

Phosphoric acid is added to the Pond 2 recycle line to promote biological growth. Because ammonia is present in the refinery wastewater, nitrogen is not added as a nutrient. Shell operates the activated sludge process to nitrify year round in order to reduce effluent ammonia concentrations. The sludge age is kept very high, especially during the winter months, to ensure the growth of nitrifying bacteria. This was evident by the dark brown mixed liquor and dark surface foam in the pond [photograph 1]. The operator on duty did not know the sludge age, stating that Shell's Quality Assurance/Quality Control (QA/QC) lab tracks sludge age along with other operating parameters. Although most operating parameters are being monitored, the operators rely on the QA/QC lab for a majority of the process control decisions.

Pond 2 effluent is pumped to two secondary clarifiers, used in parallel, for suspended solids removal. Each clarifier is 100-feet in diameter with a 15-foot side wall depth. Influent to the clarifiers flows into the center feed well where polymer is injected to aid in settling. Solids settle to the bottom and clarified wastewater overflows the outer weir to the discharge line. Sludge is withdrawn from the bottom of the clarifiers and either returned to Pond 2 or wasted to a secondary solids thickener.

The secondary gravity thickener concentrates the waste activated sludge before being sent to the solids dewatering facility. The thickener, 70-feet in diameter with a 10-foot side wall depth, can also be used as a standby clarifier if one of the secondary clarifiers is off-line. The supernatant flows over the outer weir to the clarifier effluent line.

Secondary clarifier and thickener effluent flows through a 36-inch line to the polishing lagoons, located at Shell's Hartford Docks area near the Mississippi River [photograph 2]. Treated effluent from the Village of Roxana sewage treatment plant discharges to the clarifier effluent line and is treated in the lagoons. The lagoons serve as the final treatment step before discharge, further reducing TSS and providing a cushion in the event of an upset at the WWTP. Wastewater flows into a distribution channel before entering the two polishing lagoons, which are approximately 200 feet long, 50 feet wide, and 6 feet deep. Wastewater from the two lagoons enters a channel equipped with a distribution baffle and oil boom. From there wastewater is discharged through a 36-inch outfall pipe to the Mississippi River.

The Hartford Docks area, including the polishing lagoons, was flooded by the Mississippi River for most of summer 1993 through early October 1993. The river level subsided about 2 weeks prior to the NEIC inspection. The flood washed out the sampling shed at outfall 001. Shell is taking compliance samples at outfall 002, in accordance with their NPDES permit, until the outfall 001 sampling equipment is repaired.

The solids dewatering facility is operated by Heritage, a contract operator. The facility uses three plate and frame presses, two to process primary CPI solids and the third to process secondary biological solids. About two to three truckloads of primary sludge per week are sent to an off-site landfill for disposal. About four truckloads of secondary sludge per week are sent to either of two local landfills in Edwardsville and Granite City, Illinois. All filtrate is sent back to the main lift station.

Stormwater Outfalls

Shell discharges stormwater through eight permitted outfalls (003 through 010). Only outfall 003 is associated with refinery runoff. Outfalls 004 through 010 consist of storm runoff from paved and unpaved areas located at Hartford Docks and discharge directly into the Mississippi River. Runoff from the north and east portion of Shell's property flows to Smith Lake, located on Shell property. There is no surface outlet from Smith Lake.

Outfall 003 discharges combined storm runoff to Grassy Lake from the main refinery area and from Shell's north, west, and southwest properties [photograph 3]. Grassy Lake empties into Cahokia Canal, a tributary to the Mississippi River. Refinery runoff is collected and first flush stormwater can be pumped or hydraulically routed to the process sewer system for treatment at the WWTP. Pumping occurs at the south ditch sump, which has a pump capacity of 600 to 900 gpm. North property runoff can also crossover to the process sewer at Box 6, a gravity overflow structure. Storm events generating flows in excess of the south ditch sump and/or Box 6 crossover capacities, overflow these structures and flow through a 72-inch culvert to the southwest property stormwater detention area, eventually discharging from outfall 003. The detention area also receives runoff from the southwest property tank farm.

The stormwater detention area is an earthen basin equipped with two solids screens and an underflow baffle to control the discharge of oily stormwater through outfall 003 [photograph 4]. Oil is removed periodically by vacuum trucks and returned to the refinery. Flow from the detention area discharges through two secondary basins before reaching outfall 003. The detention area appears to be filling with sediment, reducing its capacity. According to Jay Rankin, Senior Engineer, the detention area was probably constructed in the 1940s and hasn't been dredged to his knowledge. The detention area overflowed into a roadside ditch along Route 111 on April 25, 1993 after a 3-inch storm event. Oil was washed out of the detention area and flowed with the water in the ditch to outfall 003. Oil was discharged to Grassy Lake causing a sheen. Shell deployed sorbent pads and booms and collected oil with vacuum trucks to contain the release. Outfall 003 was sampled three times per day for 4 days. No exceedances of the NPDES limits for oil and grease (30 mg/L) were reported.

<u>NPDES Monitoring</u>

Shell has not been monitoring influent parameters at the appropriate location. Shell is required in their NPDES permit to monitor the WWTP influent BOD_5, TSS, pH, and ammonia concentrations twice per week (Special Condition 18). This monitoring is being conducted at the CPI system effluent, after screening, neutralization, and oil/water separation. This location is not representative of the WWTP influent, especially for measuring the pH value (because it follows neutralization). Jay Rankin, Senior Engineer, stated that the monitoring is for influent to biological treatment. However, there was no authorization from IEPA or documentation to support this.

Shell has not conducted effluent monitoring, as specified by their NPDES permit at all times. Shell is required to monitor for NPDES effluent parameters at outfall 001, the polishing lagoon effluent, during normal conditions. When outfall 001 is "impossible" to monitor due to flood conditions, Shell is authorized to monitor the effluent at outfall 002, which is the secondary clarifier and sludge thickener effluent. Flow at outfall 001 is determined by the height of water over a flow measurement weir [photograph 5]. On occasion, high river levels place the weir underwater, disabling flow measurement at outfall 001. During these instances, Shell takes the analytical sample at outfall 001 but determines flow at outfall 002. By

measuring flow at outfall 002 and collecting the compliance sample at outfall 001, Shell is reporting an inaccurate representation of the discharge through outfall 001. The loading determinations for compliance purposes may be biased high or low depending if the flow measured at outfall 002 is higher or lower then the actual flow through outfall 001. Flow measurement at outfall 002 does not include flow from Roxana's sewage treatment plant. There is no documentation as to how often this occurs. Mike Wilkey, a WWTP operator stated that it could happen each spring. This situation has not been reported on Shell's discharge monitoring reports.

Shell does not directly monitor the flow to outfall 002 for NPDES compliance. Outfall 002 includes effluent from the two secondary clarifiers and the secondary sludge thickener. Each clarifier has two magnetic meters for flow measurement: One on the influent to the clarifier and one on the recycle line to Pond 2. Shell determines the clarifier effluent flow to outfall 002 by taking the difference between the two flow measurements meters for each clarifier. This measurement will be biased high because there is no consideration for flow wasted to the sludge thickener. Flow from the sludge thickener to outfall 002 is determined by a flow meter on the sludge thickener influent line. This measurement is biased high because there is no consideration for flow sent to the solids dewatering facility.

Shell does not have a direct monitoring location when sampling outfall 002 for NPDES compliance. A composite sampler is installed to sample the clarifier effluent, but this effluent does not include the sludge thickener discharge. The sludge thickener sample is a grab sample taken by the WWTP operator by dropping a bottle into the thickener between the overflow weir and the thickener sidewall [photograph 6]. The clarifier sample and thickener sample are flow-proportioned at the QA/QC laboratory. The grab sample location is not representative of the actual thickener discharge. Jay Rankin, Senior Engineer, stated there is no feasible sample location where the thickener discharges to outfall 002. This sampling scheme was started in August 1993 because Shell's current NPDES permit requires the sludge thickener discharge to be included in outfall 002 compliance monitoring. Shell's previous permit did not include thickener discharge for outfall 002 compliance determinations. Outfall 002 compliance monitoring will also be inaccurate because of the flow measuring deficiencies.

Records/Document Review

Discharge Monitoring Reports

Discharge monitoring reports (DMRs) for the period of January 1991 through September 1993 were reviewed. The review identified the following violations: One daily maximum BOD load exceedance, two daily maximum BOD concentration exceedances, and one monthly average BOD concentration exceedance at outfall 001 (September 1991); one daily maximum chloride concentration exceedance at outfall 002 (September 1993); and two pH exceedances at outfall 003 (March 1992).

Toxicity Testing

Shell is no longer required to conduct quarterly acute toxicity testing, as required in their previous NPDES permit. Shell requested in the October 1, 1992 permit renewal application that toxicity testing be eliminated due to past testing results. Table 2 shows the acute toxicity testing results for the past 3 years. Shell cites the completion of the WWTP upgrade in 1990 as attributing to reductions in toxicity. Shell is required to perform an acute and chronic toxicity test before submittal of their next permit renewal application.

Table 2

ACUTE TOXICITY TESTING RESULTS
Shell Oil Refinery
Roxana, Illinois

Month of Test	Percent Survival in 100% Effluent
October 1990	25%
December 1990	50%
March 1991	60%
June 1991	85%
September 1991	95%
December 1991	98%
March 1992	90%
June 1992	90%
September 1992	90%
December 1992	100%
March 1993	100%
June 1993	100%

Laboratory Evaluation

A laboratory evaluation revealed numerous deficiencies with Shell's NPDES monitoring program, including inadequacies within the QA/QC program. The laboratory inspection summary and findings are discussed in a separate report titled "Laboratory Evaluation." Shell's NPDES permit states that proper operation and maintenance of facilities shall include adequate laboratory controls and appropriate quality assurance procedures. The laboratory evaluation found numerous deficiencies including: incomplete chain-of-custody procedures, daily calibration checks not performed, and method blanks not completed.

SUMMARY OF FINDINGS

Based on inspection observations, discussions with Shell personnel, and review of pertinent documentation, the following areas of noncompliance and concern, of the water pollution control requirements, were identified during the NEIC investigation.

AREAS OF NONCOMPLIANCE

35 IAC § 304.106	Visible oil was discharged to Grassy Lake on April 25, 1993.
NPDES Permit IL0000205 Special Condition 18	Shell is not conducting influent monitoring at the location required by permit. An alternate location has been used without IEPA authorization.
NPDES Permit IL0000205 Effluent Monitoring Standard Condition 10(a)	Shell has not conducted proper effluent monitoring of outfall 001, as specified by the NPDES permit when high river levels disable the 001 flow meter.
NPDES Permit IL0000205 Effluent Limitations Outfall 001	Outfall 001 DMRs document one daily maximum BOD load exceedance, two daily maximum BOD concentration exceedances, and one monthly average BOD concentration exceedance during the period of January 1991 through September 1993.
NPDES Permit IL0000205 Effluent Limitations Outfall 002	Outfall 002 DMRs document one daily maximum chloride concentration exceedance during the period of January 1991 through September 1993.
NPDES Permit IL0000205 Effluent Limitations Outfall 003	Outfall 003 DMRs document two pH exceedances during the period of January 1991 through September 1993.

NPDES Permit IL0000205 Standard Condition 5	Shell did not maintain adequate laboratory controls or appropriate quality assurance procedures including: incomplete chain-of-custody procedures, daily calibration checks were not performed, and method blanks not completed.

AREAS OF CONCERN*

- Due to decreased capacity from material deposition, Shell's stormwater detention area has the potential to overflow and impact Grassy Lake. The detention area appears to be filling with sediment, reducing its capacity. According to Jay Rankin, Senior Engineer, the detention area was probably constructed in the 1940s and has not been dredged to his knowledge. The detention area overflowed into a roadside ditch along Route 111 on April 25, 1993 after a 3-inch storm event. Oil was washed out of the detention area and flowed with the water in the ditch to outfall 003. The oil was discharged to Grassy Lake causing a sheen. Outfall 003 was sampled three times per day for 4 days. No exceedances of the NPDES limits for oil and grease (30 mg/L) were reported.

- Shell cannot accurately measure effluent flow through outfall 002. Outfall 002 includes effluent from the two secondary clarifiers and the secondary sludge thickener. Each clarifier has two magnetic meters for flow measurement: one on the influent to the clarifier and one on the recycle line to Pond 2. Shell determines the clarifier effluent flow to outfall 002 by taking the difference between the two flow meter measurements for each clarifier. This measurement will be biased high

* *Areas of concern are inspection observations of potential problems that could result in noncompliance with permit or regulatory requirements, or are areas associated with pollution prevention issues*

because there is no consideration for flow wasted to the sludge thickener. Flow from the sludge thickener to outfall 002 is determined by a flow meter on the sludge thickener influent line. This measurement is biased high because there is no consideration for flow sent to the solids dewatering facility.

- Shell does not accurately monitor the effluent for outfall 002 NPDES compliance. A composite sampler is installed to sample the clarifier effluent, but does not include the sludge thickener discharge. The sludge thickener sample is a grab sample taken by the WWTP operator by dropping a bottle into the thickener between the overflow weir and the thickener sidewall. The clarifier sample and thickener sample are flow-proportioned at the QA/QC laboratory. The grab sample location is not representative of the actual thickener discharge. Jay Rankin stated there is no feasible sample location where the thickener discharges to outfall 002. Outfall 002 compliance monitoring is also inaccurate because of the flow measuring deficiencies.

CLEAN WATER ACT
SPILL PREVENTION CONTROL AND COUNTERMEASURES

MULTI-MEDIA COMPLIANCE INVESTIGATION

SHELL OIL COMPANY
Wood River Manufacturing Complex
Roxana, Illinois

Facility Address

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Investigation Dates

October 25 through November 9, 1993

Lead Investigator

Daren Vanlerberghe, Environmental Engineer
NEIC

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MEDIA REPORT

At the request of EPA Region 5, NEIC conducted a multi-media compliance investigation of the Shell Oil Company - Wood River Manufacturing Complex (Shell), a petroleum refinery located in Roxana, Illinois. This report, one of a series that addresses investigation findings, discusses Spill Prevention Control and Countermeasure (SPCC) issues and compliance at Shell.

REGULATORY SUMMARY

Shell has greater than 1,320 gallons of aboveground oil storage capacity and, due to their location, could reasonably be expected to discharge oil into or upon the navigable waters of the United States. Therefore, Shell is required to develop and maintain an SPCC Plan. Shell has developed an SPCC Plan, which was last revised in May 1992 [Appendix A]. The plan was certified by a registered professional engineer on May 12, 1992, in accordance with 40 CFR § 112.3(d).

ON-SITE INSPECTION SUMMARY

Credentials were presented to Joseph N. Brewster, Environmental Conservation Manager, Shell. Following a general discussion of plant processes, including byproduct/waste generation and handling, a plant tour was conducted. A copy of the current SPCC plan was provided by Shell personnel. Photographs referenced in this section are contained in Appendix B. Exit conferences between regulatory and refinery personnel [Appendix C] were conducted to discuss preliminary inspection findings. NEIC personnel stressed that final determinations will be made in conjunction with regional and state personnel.

Facility Inspection/Discussions

Crude oil is delivered to the refinery through pipeline and stored at the southwest property tank farm. There are 27 crude oil storage tanks at the southwest property, most with a capacity of about 130,000 barrels. The largest tank (A-97) has a capacity of 291,000 barrels. Final products are stored at the north property tank farm. Intermediate products are stored throughout the refinery in various tank sizes. A complete tank list is contained in Appendix D.

Secondary containment for oil storage tanks in the tank farms is provided by earthen dikes, some with asphalt coated walls [photograph 1]. Most of the tanks have dedicated dikes, although some share common containment areas. The dikes are equipped with valves, which are kept closed, to control the release of liquids [photograph 2]. Stormwater collected within the dikes is manually released to the storm sewer system. North property tank drainage crosses over to the process sewer system and flows to Shell's wastewater treatment plant (WWTP). Southwest property drainage flows to a stormwater detention area. The detention area is an earthen basin equipped with an underflow baffle to control the discharge of oily stormwater to Shell's NPDES outfall 003 to Grassy Lake. The oil content of this discharge is limited to a monthly average of 15 milligrams per liter (mg/L) and a daily maximum of 30 mg/L. After draining the stormwater the valves are closed.

The majority of the drainage associated with the refinery process area is contained in the process sewer system and flows to the WWTP. Drainage or accidental spills not contained by the process sewer system will flow to the storm sewer system. Flow into the storm sewer system during dry weather and controlled drainage conditions is routed to the process sewer system.

During high storm flows, runoff from the process area flows to the stormwater detention area at the southwest property.

Shell has two tank truck loading racks, one for light oils and the other for lube products. Drainage at the light oils rack flows into a sump which is routed to the process sewer. The rack is equipped with a Scully overfill protection control system. This system also disables the truck by automatically engaging the brakes, preventing the vehicle from departing before being disconnected. Drainage at the lube rack flows to a closed sump. Oil collected in the sump can be returned to the refinery for recovery.

Tank integrity inspections are conducted by Shell, with records and results maintained by the Logistics Department. A formula sheet has been developed by Shell, based on American Petroleum Institute standards, to determine the schedule for tank inspections. The maximum inspection interval for any tank is once every 20 years. More frequent inspections occur based on tank age, previous inspection results, and other deficiencies.

The SPCC plan contains a list of equipment and materials for spill containment and cleanup maintained by Shell. Randomly selected items from the equipment list were found to be available in accordance with the plan.

In the past 3 years, Shell reported one oil spill event which impacted navigable waters. Shell reported a release on April 25, 1993 of less than 1 barrel to Grassy Lake causing an oil sheen [Appendix E]. The release occurred during a large storm event which washed out oil and water from the southwest property stormwater detention area [Photograph 3]. The oil reached Grassy Lake through outfall 003. Outfall 003 was sampled three times per day for 4 days. No exceedances of the NPDES limits for oil and grease (30 mg/L) were reported. The stormwater detention area appears to be filling with sediment, reducing its capacity. According to Jay Rankin, Senior Engineer, the detention area was probably constructed in the 1940s and hasn't been dredged to his knowledge.

Records/Document Review

Shell's SPCC Plan discusses major SPCC components without providing detail. The plan does not include a tank list or any indication of the refinery's type, location, or capacity of oil storage. The plan does not indicate the largest magnitude of spill possible or a discussion of spill history at the refinery. There is no discussion in the plan regarding incoming crude delivery or distribution of oil products. Although there is discussion regarding response personnel and communication, there is no person designated with overall responsibility for the SPCC program in the plan. Also, there are no emergency response contacts listed in the plan.

In response to several notable oil spills in the U.S., revisions to the SPCC regulations were proposed (Federal Register, Vol. 56, No. 204, October 22, 1991) to strengthen and clarify current regulatory provisions. The proposed regulations intend to provide clarification by changing current "guidelines" to requirements, particularly those provisions currently under 40 CFR § 112.7 - Guidelines for the preparation and implementation of an SPCC Plan. If the proposed regulations are adopted, Shell would have to update their SPCC Plan accordingly. The proposed regulations also include the addition of a facility notification provision.

One proposal requires diked areas for bulk containers to be sufficiently impervious to contain spilled oil for at least 72 hours. Shell may be required to improve their earthen dikes to reduce the permeability. While some dike walls are asphalt coated, the floors are not and may not be impervious to oil

for 72 hours. The current regulations state that diked areas should be "sufficiently impervious" to contain spilled oil.

The Oil Pollution Act of 1990 (OPA) requires any facility that could reasonably be expected to cause substantial harm to the environment by discharging oil into navigable waters to submit an Oil Spill Response Plan (OSRP) by February 18, 1993. Shell submitted an OSRP to EPA Region 5 on February 17, 1993. EPA had only published its proposed OSRP rules on February 17, 1993. EPA granted Shell a 2-year operating extension available under OPA.

SUMMARY OF FINDINGS

Based on inspection observations, discussions with Shell personnel, and review of pertinent documentation, the following areas of concern* of the SPCC requirements were identified during the NEIC investigation:

- Shell's stormwater detention area has the potential to overflow and impact Grassy Lake. A release occurred on April 25, 1993 during a large storm event which washed oil and water from the detention area. The oil reached Grassy Lake through Shell's NPDES outfall 003. The stormwater detention area appears to be filling with sediment, reducing its capacity. According to Jay Rankin, Senior Engineer, the detention area was probably constructed in the 1940s and has not been dredged to his knowledge.

- Shell's SPCC Plan is general, discussing major SPCC components without providing much detail. The plan does not include a tank list or any indication of the refinery's type, location, or capacity of oil storage. The plan does not indicate the largest magnitude of spill possible or a discussion of spill history at the refinery. The plan does not discuss spills associated with incoming crude delivery or distribution of oil products. Although there is discussion regarding response personnel and communication, no person is designated in the plan with overall responsibility for the SPCC program. Also, no emergency response contacts are listed in the plan.

* *Areas of concern are inspection observations of potential problems that could result in noncompliance with permit or regulatory requirements, or are areas associated with pollution prevention issues*

- If the proposed SPCC regulations are adopted, Shell would be required to update their SPCC Plan. In response to several notable oil spills in the U.S., revisions to the SPCC regulations were proposed (Federal Register, Vol. 56, No. 204, October 22, 1991) to strengthen and clarify current regulatory provisions. The proposed regulations intend to provide clarification by changing current "guidelines" to requirements, particularly those provisions currently under 40 CFR § 112.7 - Guidelines for the preparation and implementation of an SPCC Plan.

- If proposed SPCC regulations are adopted, Shell may be required to improve their earthen dikes to reduce the permeability. One proposal requires diked areas for bulk containers to be sufficiently impervious to contain spilled oil for at least 72 hours. While some dike walls are asphalt coated, the floors are not and may not be impervious to oil for 72 hours. The current regulations state that diked areas should be "sufficiently impervious" to contain spilled oil.

SAFE DRINKING WATER ACT-
UNDERGROUND INJECTION CONTROL

MULTI-MEDIA COMPLIANCE INVESTIGATION

Shell Oil Company
Wood River Manufacturing Complex
Roxana, Illinois

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D Septic Tank Replacement Permit

MEDIA REPORT

At the request of EPA Region 5, NEIC conducted a multi-media compliance investigation of the Shell Oil Company - Wood River Manufacturing Complex (Shell) located in Roxana, Illinois. This report, one of a series that addresses investigation findings, discusses Underground Injection Control (UIC) issues and compliance at Shell.

REGULATORY SUMMARY

The Safe Drinking Water Act (SDWA) established the UIC program to protect underground sources of drinking water. Discharges of substances into the subsurface are regulated under the UIC requirements of 40 CFR Parts 144, 145, and 146. The regulations divide underground injection wells into five classes (Class I through V). Class V wells include septic system wells that serve more than 20 people [40 CFR § 146.5(e)(9)]. The Illinois Environmental Protection Agency (IEPA) has been delegated the UIC program.

Shell septic systems were originally configured to discharge underground [Appendix A]. According to Jay Rankin, Senior Engineer, most drainfield discharges were rerouted by connecting the outfall piping to the process sewer system discharging to the Shell Wastewater Treatment Plant (WWTP). The septic tanks are being used as "holding" tanks and are pumped out on a regular basis.

ON-SITE INSPECTION SUMMARY

Credentials were presented to Joe N. Brewster, Manager, Environmental Conservation for Shell. Following a general discussion of the complex operations, organization, safety and environmental program, a plant tour was conducted. UIC related records/documents were reviewed. Exit conferences between regulatory and refinery personnel [Appendix B] were conducted to discuss preliminary inspection findings. NEIC personnel stressed that final determinations will be made in conjunction with regional and state personnel.

Jay Rankin, Senior Engineer, indicated that Shell has 34 active septic/sanitary systems on-site [Appendix C]. None of the septic systems/tanks have been registered with IEPA, because Shell has connected all tanks, except one, to the sanitary system and considers these holding tanks for sanitary wastes and not Class V wells. The tank for one septic system, the only system that discharges into a seepage field, was replaced in 1991 [Appendix D]. This is a county-permitted tank, and is used only occasionally during recreational activities at Kendall Hill.

Shell's maintenance facility recycles all used motor oil, and according to Mr. Rankin, used motor oil has never been disposed of in underground injection wells. Visual inspections of two sumps and one lift station (West Property) were conducted. All sumps and lift stations inspected appeared to have bottoms.

COMPLIANCE STATUS

Based on inspection observations, discussions with Shell personnel, and review of documentation, no areas of noncompliance were noted.

One area of concern was identified during the NEIC investigation. Areas of concern are inspection observations of potential problems that could result in noncompliance with permit or regulatory requirements, or are areas associated with pollution prevention issues.

- Shell has not notified IEPA and/or the city of Roxana that the facility does not have any Class V injection wells.

RESOURCE CONSERVATION AND RECOVERY ACT - HAZARDOUS WASTE MANAGEMENT

MULTI-MEDIA COMPLIANCE INVESTIGATION

Shell Oil Company
Wood River Manufacturing Complex
Roxana, Illinois

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<u>Investigation Dates</u>

October 25 through November 9, 1993

<u>Lead Investigator</u>

Linda TeKrony, Environmental Engineer
NEIC

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MEDIA REPORT

At the request of EPA Region 5, NEIC conducted a multi-media compliance investigation of the Shell Oil Company - Wood River Manufacturing Complex (Shell), Roxana, Illinois. This report, one of a series that addresses investigation findings, discusses Resource Conservation and Recovery Act (RCRA) issues (including Land Disposal Restriction regulations) and compliance at Shell.

REGULATORY SUMMARY

The refinery (EPA ID ILD080012305) generates, stores, and treats hazardous waste. A RCRA permit (No. 1191150002) was issued November 3, 1989 for storage of hazardous waste in containers. On March 22, 1991, Shell modified the RCRA Part B permit application to include four tanks for storage of hazardous waste and two surface impoundments for treatment. This modification also addressed closure of a solid waste disposal basin. In February 1993, a revision to the RCRA Part B permit application added one tank to replace the four tanks added in the March 1991 revision. In September 1993, the RCRA Part B permit was modified requesting delayed closure for two treatment surface impoundments. The modification requested that the final closure of the surface impoundment be delayed until after March 1994. This request has not been formally granted by U.S. EPA.

Two RCRA complaints have been initiated by the Illinois Environmental Protection Agency (IEPA) against Shell. (Neither complaint has officially been filed.) The first complaint outlines violations that resulted from the storage of refractory brick containing lead for longer than 90 days. The second complaint outlines violations resulting from the disposal of lime sludge filter cake containing benzene at an off-site non-RCRA facility. Settlements for both complaints are being negotiated by IEPA and Shell.

ON-SITE INSPECTION SUMMARY

Credentials were presented to Joe Brewster, Manager, Environmental Conservation, Shell. Following a general discussion of refinery processes, including byproduct/waste generation and handling, a refinery tour was conducted. The following refinery areas were inspected: Generation points, spent catalyst less-than-90-day accumulation area, permitted storage building, wastewater treatment plant (WWTP), and the primary solids dewatering facility. Records/documents affiliated with the regulated activity were also reviewed. Photographs are provided in Appendix A. Exit conferences between regulatory and refinery personnel [Appendix B] were conducted to discuss preliminary inspection findings. NEIC personnel stressed that final determinations will be made in conjunction with regional and state personnel.

Hazardous Waste Generation

Shell generates at least 1,000 kilograms per month of hazardous waste. Wastes are accumulated at generation points, less-than-90-day accumulation areas, and a permitted storage facility (CATCO building). Hazardous waste generated throughout the refinery includes: primary solids, dissolved air flotation (DAF) floats, slop oil emulsions, reactor catalysts, and sulfolane bearing water [Table 1].

Table 1

SOLID WASTE GENERATED
Shell Oil Refinery
Roxana, Illinois

Department	Plant or Unit	Solid Waste Generated	EPA Hazardous Waste Number (if applicable)
Distilling/Gas	Sour water stripper system	Filters	
Cracking/Alkylation	Alkylation unit	Sulfuric acid	
	Benzene extraction unit	Sulfolane bearing water Filters Clay contactors	
	Catalytic cracking units	Reactor catalyst	
	Catalytic hydrotreater	Reactor catalyst	D001
Hydroprocessing	Catalytic reformers	Reactor catalyst	
	Distillate hydrotreaters	Reactor catalyst	D001
	Hydrocracker	1st stage catalyst 2nd stage catalyst	D001 D001
	Hydrodesulfurization units	Reactor catalyst	
	Kerosene hydrotreater	Reactor catalyst	D001
	Saturates gas plant	Diethanolamine	
	Steam methane reformer	High temperature shift catalyst Low temperature shift catalyst Reformer catalyst Methanator catalyst Zinc oxide	D001 D001 D001

Table 1 (continued)

Department	Plant or Unit	Solid Waste Generated	EPA Hazardous Waste Number (if applicable)
Lubricants	Catalytic dewaxing unit	Dewax catalyst Hydrotreating catalyst Drying material	D001
	Hydrotreater	Reactor catalyst	D001
Miscellaneous	Sulfur plant	Claus 1st stage catalyst Claus 2nd stage catalyst SCOT catalyst Charcoal filter	
	Miscellaneous	Slop oil emulsions Leaded tank bottoms Heat exchanger cleaning sludge Primary solids Filter cloths from primary solids presses Used personnel protective equipment Bar screen debris Lead contaminated paint waste	D001, D018, K049 K052 K050 F037, F038 F037, F038 F037, F038 F037, F038 D008

Facility Inspection/Discussion

Generation Points (Satellite Accumulation Areas)

At the time of the NEIC inspection, no satellite accumulation areas were located at the North Property. The maintenance shops have changed to degreasers that are not listed hazardous wastes and do not meet the definition of an ignitable characteristic hazardous waste.

Two satellite accumulation areas are located at the West Property. One 55-gallon drum is used to accumulate hazardous waste filter cloths from the solids dewatering facility. The second satellite accumulation area consists of a 55-gallon drum used to accumulate contaminated personal protective equipment. Both wastes collected in the satellite accumulation areas are contaminated with primary solids (EPA hazardous waste number F037). When the drums are full, they are transported to the CATCO building, on the North Property.

Spent Catalyst Less-Than-90-day Accumulation Area

Approximately 250 flow bins of spent catalyst were stored at a less-than-90-day accumulation area. The flow bins contained spent catalyst generated during a recent turn around [Table 2]. One hundred and seventy flow bins containing hazardous waste were improperly labeled. The bins were marked "Waste Pyrophoric Solids," not "Hazardous Waste" [photographs 1 through 6]. Each bin was labeled with a white label that contained a description of the contents of the flow bin and the date of generation.

Table 2

HYDROPROCESSING SPENT CATALYST FLOW BINS
Shell Oil Refinery
Roxana, Illinois

Area of Generation*	Number of Flow Bins	Date of Generation	H=Hazardous Waste N=Nonhazardous Waste
A	78	10-01-93	H
B	6	08-06-93	N
C	8	08-05-93	H
D	11	10-18-93	H
E	38	10-04-93	H
F	3	10-01-93	H
G	32	08-11-93	H
H	75	10-18-93	N

* *Specific reactors and processes were claimed Confidential Business Information by Shell personnel.*

Permitted Storage Building

The permitted storage building, called the CATCO building, was permitted by IEPA effective November 3, 1989. The CATCO building is a totally enclosed building, permitted to store up to 22,000 gallons of hazardous waste in containers. On October 27, 1993, 32 drums of hazardous waste were stored in the CATCO building [Table 3]. The permit requires that all containers stored in the CATCO building are marked with: the name of the waste stream, the EPA hazardous waste number, the waste group number (as defined in the permit), the container identification number (as defined in the permit), and the hazardous characteristic of the waste. Two 55-gallon drums were not labeled with the EPA hazardous waste number [photographs 7 and 8]. Sixteen 55-gallons drums were not marked with the waste group number

Table 3

DRUMS STORED IN CATCO BUILDING
Shell Oil Refinery
Roxana, Illinois

Waste Stored	Number of Drums	Date of Accumulation	EPA Hazardous Waste Numbers
Lead contaminated material	1	08-21-93	D008
Sulfolane filters	4	09-08-93	D018
Sulfolane filters	8	10-01-93	D018
Sulfolane filters	4	10-11-93	D018
Filter cloths from press 2 & 3	5	05-10-93	F037, F038, D018
PPE[1] contaminated with F037, F038 waste	1	06-16-93	F037, F038, D018
Used PPE	1	08-10-93	F037, F038
Used PPE	1	08-03-93	F037, f038
Used PPE	1	08-11-93	F037, F038
Used PPE	1	09-14-93	F037, F038
Used PPE	1	08-14-93	F037, F038
Used PPE	1	08-18-93	F037, F038
PPE contaminated with F037, F038 waste	1	07-08-93	F037, F038
Digestion solution for C.O.D.	1	05-25-93	No EPA hazardous waste number
Mercury and mercury contaminated debris	1	08-05-93	No EPA hazardous waste number

1 *Personal Protective Equipment*

and none of the drums in storage (32) were marked with a container identification number. Eric Petersen, Process Engineer, indicated that the facility has never assigned container identification numbers to the drums as they are placed in the CATCO building.

Wastewater Treatment Plant

Shell's wastewater treatment plant (WWTP) consists of screening, neutralization, oil/water separation [Corrugated Plate Interceptor (CPI) separators], DAF thickening, equalization, biological treatment, clarification, and polishing. Three hazardous waste streams are generated at the WWTP: Bar screen debris, slop oil emulsions, and primary solids including CPI separator solids and DAF floats.

Bar screen debris is generated at the beginning of treatment, where large material is removed from the influent to the WWTP. This waste stream is collected in two less-than-90-day bins, with approximately one to two bins of bar screen debris generated each month. The two bins were not labeled with the words "Hazardous Waste" or dated [photograph 9]. Bar screen debris is manifested off-site for incineration as EPA hazardous waste number F037.

CPI separator solids, DAF floats, and slop oil emulsions are all fed to tanks D-52 and D-53. These tanks are used to break up emulsions that form during wastewater treatment, and are exempt from RCRA Subtitle C regulation because they are part of the wastewater treatment plant. Tank D-54 is used to chemically break emulsions that have not responded to treatment in the other two tanks. Solids from the slop oil emulsion tanks are dewatered at the solids dewatering facility (Heritage). Slop oil emulsions that cannot be broken up are manifested off-site as EPA hazardous waste number K049.

Two surface impoundments are operated as part of the WWTP. Neither pond complies with the minimum technical requirements for surface impoundments. Pond 1 is used as an equalization basin, and pond 2 consists of aerated biological treatment. Both surface impoundments are currently operating under RCRA interim status. Pond 1 generates primary solids (EPA hazardous waste number F037) and pond 2 receives wastewater containing benzene above the Toxicity Characteristic Leaching Procedure (TCLP) regulatory level of 0.5 parts per million (ppm).

Shell is in the process of upgrading the WWTP. An equalization tank will be built to replace pond 1. Shell has applied to delay the closure of pond 1 in order to allow for continued operation of the unit in nonhazardous waste service after the required upgrade or closure date of March 29, 1994. Once the new equalization tank is operational, pond 1 will be used as an emergency diversion unit. Shell also applied to IEPA to delay the closure of pond 2. Pond 2, under interim status, treats wastewater that is a hazardous waste because the benzene concentration in the influent is above the toxicity characteristic regulatory limit. By adding a new stage of biological treatment before pond 2, Shell believes that the influent to pond 2 will contain less than the TCLP regulatory level of 0.5 ppm benzene. Pond 2 will continue to be operated as a biological treatment unit after the new stage of biological treatment is constructed. In the application, Shell states that the continued operation of the two surface impoundments will be necessary, even after the modifications to the WWTP, to meet the National Pollutant Discharge Elimination System permit requirements.

Solids Dewatering Facility

Solids generated at the WWTP are sent to the solids dewatering facility (Heritage). Hazardous waste solids (primary solids including CPI separator solids and DAF floats), as well as waste activated sludge (biosludge), are dewatered at the Heritage facility; however, separate equipment is used for the two different solids. Approximately one to two trailer loads (16 to 34 tons) per week of hazardous waste dewatered primary solids are generated. Primary solids from the WWTP are pumped to Heritage and stored in two tanks (No. T-1 and T-2). These tanks were labeled "Waste Surge" [photograph 10]. The solids from tank T-1 and T-2 are discharged to a mix tank where perlite (a water absorbing compound) is added. Two additional tanks (Nos. T-6 and T-7) are used to collect oil that separates from the primary solids. The oil is returned to the refinery for further processing, and any water is discharged to the influent of the WWTP. After the perlite is added, the solids are dewatered in plate and frame presses. The dewatered solids are dropped into truck trailers. At the time of the NEIC inspection, the truck trailers were labeled with "Hazardous Waste" labels. The primary solids are currently manifested off-site (EPA hazardous waste numbers F037 and F038) for incineration. The filter cloths from the presses are collected in 55-gallon drums and stored in the CATCO building prior to being manifested off-site for incineration.

Prior to 1988, solids from the wastewater treatment plant were disposed of on-site at the Solid Waste Disposal Basin. This practice was discontinued in the fall of 1988 due to the Land Disposal Restrictions being promulgated. Dewatering of solids from the wastewater treatment plant, including DAF solids and Association of Petroleum Institute (API) separator sludge, was begun at this time. At the end of 1990, modifications to the wastewater treatment plant were begun which included replacing the API separator with a CPI separator, and discharging the DAF floats to the oil recovery tanks. Eric Petersen, Process Engineer, stated that due to the equipment change, the EPA hazardous waste code applicable to the waste being generated was F037 and F038. In June 1993, the solids from the wastewater treatment plant were dewatered and manifested off-sent to a cement kiln.

Biosludge is dewatered in one plate and frame press. The dewatered biosludge is sent to either of two local landfills in Edwardsville and Granite City, Illinois.

Shell has submitted an application to IEPA for a project to blend hazardous waste primary solids from the wastewater treatment plant with catalytic cracker slurry oil. The primary solids consist of CPI separator solids, DAF floats, and solids from the slop oil emulsion tanks. The catalytic cracker slurry oil is a low value product, currently being converted into No. 6 fuel oil. The hazardous waste primary solids/oil mixture will be manifested to a cement kiln as a hazardous waste fuel.

Heritage personnel wear personal protective equipment [PPE] (tyvex suits, gloves, and half-face respirators) when they are removing the dewatered solids from the presses. Used PPE was disposed of in the truck trailer and incinerated with the primary solids. Because Shell is beginning the hazardous waste fuel project, the used PPE has been collected in 55-gallon drums. At the time of the NEIC inspection, eight drums of contaminated PPE (EPA hazardous waste numbers F037 and F038) were stored in the CATCO building on the Main Property. The Heritage dewatering facility is located in the West Property. Eric Petersen, Process Engineer, indicated that the drums were transported to the Main Property from the West Property by a Shell truck along Route 111 (a public highway). Mr. Petersen also stated that the drums were not manifested to the Main Property. The West Property has not been assigned an EPA Identification Number. The EPA Identification Number for the Main Property has been used to complete the manifests for the primary solids that are generated at the West Property [Appendix C].

Sewer System

Process wastewater discharged to the sewer system contains benzene above the toxicity characteristic regulatory level for a characteristic hazardous waste. NEIC collected and analyzed four samples (two taken on November 3, 1993 and two taken on November 4, 1993) from the master box. The master box is a sampling point, on the Main Property, where all process waste streams combine. Sample analytical results [Appendix D] show that wastewater sampled from the master box is a RCRA characteristic hazardous waste for the toxicity characteristic of benzene. The sample results range from 2.7 ppm to 3.7 ppm. Various portions of the sewer have been replaced in the past due to leaks in the lines. Because there have been leaks in the sewer lines in the past, hazardous waste may have been disposed.

Lime Sludge Dewatering Facility

Cooling tower water is treated with lime to soften the water prior to use. The water is pumped from a well field located near the North Property, where the groundwater has been contaminated with hydrocarbons from past practices and spills. The lime sludge that forms from the treatment of cooling tower water contains varying amounts of hydrocarbons including benzene. The amount of benzene in the lime sludge directly correlates to the amount of hydrocarbons pumped out of the subsurface along with the water. In June and July 1992, Shell shipped 12 loads of lime sludge filter cake that contained more than the TCLP regulatory limit of 0.5 ppm benzene to a nonhazardous waste landfill. IEPA issued a complaint for violations, and is currently working with Shell to finalize the issue.

Since July 1992, Shell has modified the procedures for disposal of lime sludge filter cake in order to verify that only nonhazardous lime sludge filter

cake is disposed of at nonhazardous landfills. The procedure now in place includes: keeping free phase oil out of the water pumped for treatment, analyzing the lime sludge for TCLP benzene instead of total benzene, and attaching a copy of the analysis for each load to the special waste (IEPA terminology) manifest before shipment. According to Eric Petersen, Process Engineer, only two loads of lime sludge filter cake have contained more then the TCLP regulatory limit of 0.5 ppm of benzene since the new procedure was implemented. These two loads were manifested off-site as hazardous waste.

Sulfolane-Bearing Water Tanks

Shell currently operates one hazardous waste storage tank for sulfolane-bearing water. This waste stream is a characteristic hazardous waste due to the toxicity characteristic of benzene. Sulfolane is a solvent used in the benzene extraction unit to preferentially remove benzene from an intermediate stream. The sulfolane and benzene are separated using water. Sulfolane bearing water is manifested to Safety-Kleen for the recovery of the sulfolane. The recovered sulfolane is returned to Shell for reuse.

Prior to 1992, four tanks were used for the storage of sulfolane bearing water. The tanks were emptied, and the sludges dewatered and manifested off-site as hazardous waste. The tank shells were cut up, decontaminated, and shipped to scrap metal dealer, Recycling Associated Services, of Mt. Vernon, Illinois. Shell and IEPA have agreed to clean-up objectives; however, Shell is waiting for an EPA Region 5 decision regarding Shell's plan for final closure. Shell has proposed to remove several feet of soil, cap the area, and address any groundwater contamination under the current refinery-wide groundwater remediation plan.

Cooling Towers

Shell operates several cooling towers throughout the facility. Chromate is still used in the towers, which can generate a hazardous waste sludge. Shell has no immediate plans to discontinue use of chromate.

Records/Document Review

Manifests and Land Disposal Restriction Notifications

Shell personnel provided manifests retained on-site for the years 1992 and 1993. In excess of 750 hazardous waste manifests and associated Land Disposal Restriction (LDR) notifications, from January 1992 through September 1993, were reviewed. Numerous LDR notification deficiencies were found [Appendix E]. The manifests are included in Volume 3.

LDR notifications for primary solids and slop oil emulsions do not include all the applicable EPA hazardous waste numbers. Primary solids from the dewatering facility are manifested off-site with EPA hazardous waste numbers F037 and F038. The solids that are sent to the dewatering facility come from tanks D-52, D-53, and D-54, which include DAF floats. None of the manifests or LDR notifications (after November 1992) reviewed for primary solids included the EPA hazardous waste number for DAF floats (K048). Slop oil emulsions, generated in tank D-54, that are manifested off-site also do not include the EPA hazardous waste number K048. A total of 91 LDR notifications did not include the EPA hazardous waste number K048.

Thirty-three LDR notifications for slop oil emulsions did not include the correct treatment standards for K049. In general, the notifications included a treatment technology, not the treatment standards for K049. The treatment

standards for K048, as discussed above, were also not included on these LDR notifications.

Prior to November 1992, LDR notifications for EPA hazardous waste number K048 were required to be sent to the treatment or storage facility. Between January 1992 and March 1992, 88 manifests for primary solids did not include LDR notifications.

SUMMARY OF FINDINGS

AREAS OF NONCOMPLIANCE

Based on inspection observations, discussions with Shell personnel, and review of documentation, the following areas of noncompliance of the hazardous waste management requirements, including Title 35 of the Illinois Administrative Code (IAC), were identified.

35 IAC § 722.134(a)(3) [40 CFR § 262.34(a)(3)]	The following containers were not labeled or marked with the words "Hazardous Waste." • One hundred and seventy flow bins of spent catalyst • Two bins of bar screen debris
RCRA Permit 1191150002 J.3	Drums stored in the CATCO building were not properly marked. • Two drums were not marked with the EPA hazardous waste number • Sixteen drums were not marked with the waste group number • Thirty-two drums were not marked with a container identification number
35 IAC § 722.134(a)(2) [40 CFR § 262.34(a)(2)]	Two bins of bar screen debris were not marked with the date upon which each period of accumulation begins.
35 IAC § 722.120(a) [40 CFR § 262.20(a)]	Eight drums of hazardous waste were not manifested from the West Property to the Main Property. The hazardous waste is transported along a public road from the West Property to the Main Property.

35 IAC § 722.112(a) [40 CFR § 262.12(a)]	Hazardous waste has been offered for transportation from the West Property without Shell receiving an EPA Identification Number.
35 IAC § 728.107(a)(1) [40 CFR § 268.7(a)(1)]	Ninety-one primary solids and slop oil emulsion LDR notifications were incomplete or incorrect. Missing or incorrect information included: treatment standards and EPA hazardous waste numbers.
35 IAC § 728.107(a)(1) [40 CFR § 268.7(a)(1)]	Eighty-eight LDR notifications were not sent to the treatment or storage facility with the waste shipment.

AREA OF CONCERN

The following area of concern* with the hazardous waste management regulations was identified.

- Process wastewater discharged to the sewer system contains benzene above the toxicity characteristic regulatory level for a characteristic hazardous waste, and may have leaked into the surrounding soil. NEIC collected and analyzed two samples (November 3 and 4, 1993) from the master box. The master box is a sampling point, on the Main Property, where all process waste streams combine. Sample analytical results show that wastewater sampled from the master box is a RCRA characteristic hazardous waste for the toxicity characteristic of benzene. The sample results range from 2.7 ppm to 3.7 ppm.

* *Areas of concern are inspection observations of potential problems that could result in noncompliance with permit or regulatory requirements, or are areas associated with pollution prevention issues.*

Various portions of the sewer have been replaced in the past due to leaks in the lines. Because there have been leaks in the sewer lines in the past, hazardous waste may have been disposed.

RESOURCE CONSERVATION AND RECOVERY ACT -
UNDERGROUND STORAGE TANKS

MULTI-MEDIA COMPLIANCE INVESTIGATION

Shell Oil Company
Wood River Manufacturing Complex
Roxana, Illinois

Facility Address

Shell Oil Company
Wood River Manufacturing Complex
Highway 111
Roxana, Illinois 62084
(618) 255-2478

Investigation Dates

October 25 through November 9, 1993

Lead Investigator

Linda TeKrony, Environmental Engineer
NEIC

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MEDIA REPORT

At the request of EPA Region 5, NEIC conducted a multi-media compliance investigation of the Shell Oil Refinery - Wood River Manufacturing Complex (Shell), a petroleum refinery in Roxana, Illinois. This report, one of a series that addresses investigation findings, discusses Underground Storage Tank (UST) issues and compliance at Shell.

REGULATORY SUMMARY

Shell provided an updated notification to the Illinois State Fire Marshal on October 9, 1990 including two USTs for used oil, five for diesel fuel, one for lube oil, seven for oil-based additive, one for naphthenic acid, four for gasoline, and one for acetone [Table 1]. Shell has closed all USTs that operated on-site, and currently have none in operation.

ON-SITE INSPECTION SUMMARY

Credentials were presented to Joe Brewster, Manager, Environmental Conservation, Shell. Following a general discussion of plant processes, including byproduct/waste generation, a general plant tour was conducted. Shell UST related records/documents were reviewed, including notifications and information of tank removals. Exit conferences between regulatory and refinery personnel [Appendix A] were conducted to discuss preliminary inspection findings. NEIC personnel stressed that final determinations will be made in conjunction with regional and state personnel.

Shell currently has no USTs in operation. The last operating UST was removed in February 1991. Nine inoperable USTs remain in the ground, filled with sand. Ten USTs were removed from the ground in November 1989, prior to applicability of the leak detection requirements.

Table 1

UNDERGROUND STORAGE TANKS
Shell Oil Refinery
Roxana, Illinois

Tank Number	Date Installed	Size (gallons)	Material Stored	Date Removed
CH-211	1950	1,500	Used oil	10-30-89
I-6	1949	12,800	Diesel fuel	10-27-89
I-7	Unknown	12,800	Diesel fuel	11-1-89
I-11	Unknown	11,200	Diesel fuel	11-1-89
4	Unknown	600	Diesel fuel	11-9-89
N-95	Unknown	10,600	Lube oils	January 1983*
N-97	Unknown	10,600	Oil-based additives	January 1983*
N-99	Unknown	10,600	Oil-based additives	January 1983*
N-100	Unknown	10,600	Oil-based additives	January 1983*
N-101	Unknown	10,600	Naphthenic Acid	January 1993*
N-102	Unknown	10,300	Oil-based additives	January 1983*
N-103	Unknown	10,600	Oil-based additives	January 1983*
N-108	Unknown	10,600	Oil-based additives	January 1983*
N-109	Unknown	10,600	Oil-based additive	January 1983*
RR-41	1963	2,100	Gasoline	10-23-89
RR-42	1963	6,200	Gasoline	10-20-89
RR-43	1966	6,200	Gasoline	10-19-89
1	1953	600	Gasoline	11-14-89
2	1953	700	Used Oil	11-8-89
3	1963	700	Diesel fuel	11-6-89
V-1707	1942	1,700	Acetone	February 1991

* *Tank was emptied, filled with sand, and left in place.*

UST V-1707 was discovered in September 1990. The Illinois State Fire Marshal was notified of the existence of V-1707 in October 1990 [Appendix B]. Facility personnel indicated that the UST was removed from service in February 1991. At the time of discovery, the tank was empty and reportedly not used since June 1980.

COMPLIANCE STATUS

Based on discussions with Shell personnel and review of available documents, Shell has no underground storage tanks in service. Shell removed from service 10 USTs in November 1989, and 1 in February 1991. No other USTs were identified during the NEIC on-site inspection.

EMERGENCY PLANNING AND COMMUNITY RIGHT-TO KNOW ACT

MULTI-MEDIA COMPLIANCE INVESTIGATION

Shell Oil Refinery
Wood River Manufacturing Complex
Roxana, Illinois

Facility Address

Shell Oil Company
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Anne Bevington, Chemical Engineer
NEIC

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MEDIA REPORT

At the request of EPA Region 5, NEIC conducted a multi-media compliance investigation of the Shell Oil Refinery - Wood River Manufacturing Complex (Shell) located in Roxana, Illinois. This report, one of a series that addresses investigation findings, discusses Emergency Planning and Community-Right-to-Know Act (EPCRA) issues and compliance at Shell.

REGULATORY SUMMARY

The Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) was enacted in 1980. Provisions in CERCLA require facilities to report releases of hazardous substances in excess of reportable quantities to the National Response Center. Chevron is subject to the Designation, Reportable Quantities, and Notification requirements of 40 CFR Part 302 (CERCLA § 103).

EPCRA was enacted as Title III of the Superfund Amendments and Reauthorization Act (SARA) of 1986. EPCRA (also known as SARA Title III) requires regulated facilities to provide information to EPA, state, and community groups concerning chemicals handled by the facility and chemical releases. Shell is subject to: the Designation, Reportable Quantities, and Notification requirements of 40 CFR Part 302; the Emergency Planning and Notification requirements of 40 CFR Part 355; the Hazardous Chemical Reporting: Community Right-to-Know requirements of 40 CFR Part 370; and the Toxic Chemical Release Reporting requirements of 40 CFR Part 372. The EPCRA regulations are referenced by the Illinois Emergency Planning and Community Right to Know Act of the Illinois Revised Statutes, Chapter 111 1/2.

Region 5 filed an Administrative Complaint against Shell in December 1992, for alleged violations of CERCLA § 103 and EPCRA § 304. Between February 16, 1989 and August 9, 1990, Shell had nine significant releases that were not reported or were reported late to the appropriate response authorities. Shell is currently in negotiations with Region 5 in regard to this complaint.

ON-SITE INSPECTION SUMMARY

Credentials were presented to Joe Brewster, Manager Environmental Conservation for Shell. Following a general discussion of plant processes, including byproduct/waste generation and handling, the EPCRA related records/documents were reviewed. Exit conferences between regulatory and refinery personnel [Appendix A] were conducted to discuss preliminary inspection findings. NEIC personnel stressed that final determinations will be made in conjunction with regional and state personnel.

Emergency Notification Reporting [CERCLA §103 and EPCRA §304 (a) and (c)]

Shell has developed procedures to report hazardous spills and releases. For all spills or releases, procedures indicate the foreman of the process area immediately notifies an Environmental Supervisor. Shell has five Environmental Supervisors who rotate shifts and are on call 24 hours per day. The supervisor then fills out an incident report and makes the required telephone notifications. Shell incident reports include:

- Material and amount released
- Agencies notified
- Date and time agencies were notified
- A brief description as to the cause of the spill
- A brief description of any response actions

The Shell spill and release file was reviewed. Nineteen releases exceeding the reportable quantities [Appendix B] were reported to the National Response Center (NRC) from August 21, 1990 through May 16, 1993 [Table 1].

Provisions in the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) § 103 require facilities to immediately notify the NRC of any hazardous substance releases to the environment in excess of the reportable quantities. (Federally permitted releases are excluded from this reporting requirement.) Shell's notification to NRC for 12 nonpermitted reportable releases was not made immediately [Table 1].

Provisions in EPCRA § 304 require facilities to immediately notify the local emergency planning committee and the state emergency response commission of any hazardous substance releases to the environment in excess of the reportable quantities. The state emergency response commission and the local emergency planning committee were not immediately notified of 12 reportable releases. This section also requires a written follow-up emergency notification for releases of extremely hazardous substances above the reportable quantity. The required follow-up notifications for all extremely hazardous substance releases were provided by Shell within 3 weeks of the incident.

Shell does not report all releases above the reportable quantity. The 1,000 parts per million SO_2 emission limit for the sulfur recovery unit (SRU) was exceeded on 28 occasions from February 1991 through October 1993. During the excess emissions, the quantity of SO_2 released ranged from 25 pounds to 1,576 long tons. The operating permit for the SRU allows excess emissions provided that the Illinois Environmental Protection Agency is notified immediately. Shell considers these incidents permitted releases and does not report them to the state and local emergency committees.

Table 1

EMERGENCY RELEASE NOTIFICATIONS
Shell Oil Company
Roxana, Illinois

Date	Time	Compound	Amount (lbs)	Hazardous/ Extremely Hazardous	Notifications				
					NRC	Local LERC	State ESDA	IEPA	Follow-up Notification
8/21/90	1:00p	NaOH	2,000	Hazardous	2:35p	2:50p	2:39p	---	9/7/90
12/22/90	6:15a	H_2S	200	EHS	9:12a*	9:19a	9:21a	9:40a	1/17/91
12/23/90	9:10p	H_2S	1,500	EHS	9:45a* 12/24/90	9:50a 12/24/90	9:45a 12/24/90	11:32a 12/23/90	1/17/91
1/1/91	5:30a	H_2S	140	EHS	9:00a*	9:15a	9:07a	9:58a	1/17/91
1/20/91	7:00p	NaOH	9,300	Hazardous	9:25p*	9:32p	9:30p	10:45p	2/8/91
1/28/91	5:50p	H_2S	3,000	EHS	6:45p	7:11p	6:52p	7:32p	2/13/93
5/10/91	5:20p	H_2SO_4	200,000	Hazardous	6:43p	7:08p	6:55p	12:08a 5/11/91	5/21/91
5/20/91	6:50a	Benzene	26	Hazardous	12:45p*	1:00p	12:53p	1:13p	6/4/91
9/8/91	3:30a	NaOH	1,800	Hazardous	9:01a*	9:32a	9:13a	10:30a	9/18/91
12/5/91	9:58p	Benzene	5,000	Hazardous	11:21p	11:48p	11:32p	12:34a 12/6/91	12/23/91
12/20/91	10:14a	Benzene	20	Hazardous	1:02p*	1:31p	1:07p	1:26p	1/20/92
1/15/92	9:00a	Chlorine	600	EHS	10:13a	10:27a	10:31a	10:20a	1/28/92

* *Indicates a spill that was not immediately reported to the National Response Center or the local and state authorities.*

Table 1 (continued)

Date	Time	Compound	Amount (lbs)	Hazardous/ Extremely Hazardous	Notifications				
					NRC	Local LERC	State ESDA	IEPA	Follow-up Notification
3/28/92	3:45p	Chlorine	500	EHS	7:55p*	8:01p	8:10p	8:50p	4/13/92
10/18/92	11:30p	H_2S	1,200	EHS	1:26a 10/19	1:41a 10/19	1:36a 10/19	1:50a 10/19	11/2/92
10/18/92	11:30p	Methyl mercaptan	1,200	EHS	1:26a 10/19	1:41a 10/19	1:36a 10/19	1:50a 10/19	11/2/92
1/18/93	7:15a	H_2SO_4	1,100	EHS	10:09a*	10:22a	10:16a	10:31a	1/26/93
2/23/93	3:00p	H_2S	280	EHS	6:10p*	6:15p	6:25p	6:57p	3/2/93
2/23/93	3:00p	Ammonia	110	EHS	6:10p*	6:15p	6:25p	6:57p	3/2/93
5/16/93	12:30p	H_2S	200	EHS	4:17p*	5:00p	4:23p	5:05p	5/28/93

* *Indicates a spill that was not immediately reported to the National Response Center.*

Emergency Planning Notifications (EPCRA § 302 and 303)

Notification was provided on April 28, 1987 to the Illinois Emergency Services & Disaster Agency (ESDA) that the refinery handles extremely hazardous substances in excess of the threshold planning quantities identified in the regulations. The Madison County Local Emergency Planning Committee (LEPC) was notified on August 10, 1987 of the refinery's designated emergency coordinator, Mr. R.C. Newall. The committee, Illinois ESDA, and the fire department are notified of changes in the designated emergency coordinator.

Community Right-to-Know Requirements (EPCRA § 311 and 312)

Shell submits a Tier II inventory in lieu of a Tier I inventory to the Illinois ESDA, Madison County LEPC, and the Hartford County Fire Departments. The inventory is updated and submitted to each agency on an annual basis.

Shell maintains copies of MSDSs in each operational area and at the Health and Safety department. Health and Safety maintains an on-line computer system to track all materials coming into the facility and updates the MSDS listing on an ongoing basis as materials are ordered. Shell's corporate office also has an MSDS listing for the facility. An updated MSDS list is submitted to the Illinois ESDA, Madison County, and the fire departments on an annual basis.

Toxic Release Inventory Reporting (EPCRA § 313)

Shell has submitted the Toxic Chemical Inventory Reporting Forms (Form Rs) for chemicals that were present in amounts above the threshold planning levels. Shell reported that approximately 900,000 pounds (total) of

chemicals were released from the refinery during 1992. The chemicals reported on Form Rs from 1987 through 1991 are:

- aluminum oxide
- ammonia
- benzene
- 1,3-butadiene
- butyl benzyl phthalate
- chlorine
- chromium
- cobalt
- copper
- cresol
- cumene
- cyclohexane
- 1,2-dibromoethane
- 1,2-dichloroethane
- diethanolamine
- ethylbenzene
- ethylene
- ethylene glycol
- glycol ethers
- hydrochloric acid
- lead
- manganese
- methanol
- methyl tert butyl ether (MTBE)
- molybdenum trioxide
- naphthalene
- nickel
- phenol
- phenylenediamine
- phosphoric acid
- propylene
- sodium hydroxide
- sulfuric acid
- toluene
- 1,1,1-trichloroethane
- 1,2,4-trimethyl benzene
- xylene
- zinc

Significant changes (increases or decreases) in the yearly chemical releases were discussed with Shell personnel. A summary of the 1987 through 1992 Form R submittal is presented in Table 2. Shell uses a combination of emission factors (fugitive air), analytical results (water), material balances, stack tests (air), and hazardous waste manifests (land disposal and off-site transfers) to calculate reported quantities. A data base program is used to assemble the annual emission estimates. Spills and uncontrolled releases are also incorporated into the annual emission estimates. Review of the 1987 through 1992 Form R submittal and calculation methods used to determine emission estimates resulted in the following observations:

Table 2

SUMMARY OF FORM R SUBMITTALS 1988, 1989,1990, 1991 AND 1992
Shell Oil Refinery
Roxana, Illinois

Chemical	Quantity Released (pounds)				
	1988	1989	1990	1991	1992
Aluminum Oxide					
Releases					NR[1]
Stack air	200,000	0	0	0	
Land	660,000	0	0	0	
Transfers					
Off-site	230,000	0	0	0	
Ammonia					
Releases					
Fugitive air	0	30	0	0	3,700
Stack air	250	180,000	220,000	170,000	170,000
Water	442,800	281,500	190,670	87,100	65,400
Land	250	0	0	0	0
Transfers					
Off-site	34	68	68	67	0
Benzene					
Releases					
Fugitive air	200,000	190,000	190,000	160,000	270,000
Stack air	79,000	74,000	55,000	58,000	18,000
Land	110	33,000	0	0	0
Transfers					
Off-site	9	359	479	7,400	5,648
1,3-Butadiene					
Releases					
Fugitive air	1,800	1,500	1,400	150	230
Butyl Benzyl Phthalate					
Releases	0	0	0	0	NR
Chlorine					
Releases					
Fugitive air	0	5	0	10	0
Stack air	0	0	0	0	1,100
Chromium					
Releases					
Fugitive air	12,000	11,000	11,000	11,000	10,000
Water	1,900	2,158	2,526	2,140	2,330
Land	17,000	0	0	0	0
Transfers					
Off-site	7,300	22,560	21,957	23,122	31,030
Cobalt					
Releases	0	0	0	0	0
Transfers					
Off-site	0	0	0	0	14,840

1 *10,000 pound threshold level was not exceeded, therefore a Form R was not submitted.*

Table 2 (continued)

Chemical	Quantity Released (pounds)				
	1988	1989	1990	1991	1992
Copper					
Releases	0	0	0	0	NR[1]
Cresol					
Releases					
Fugitive air	0	0	0	0	1,100
Stack air	250	0	0	0	51
Land	7	0	0	0	0
Cumene					
Releases					
Fugitive air	0	0	0	2,500	6,600
Stack air	0	0	0	1,700	1,200
Water	0	0	0	1	0
Transfers					
Off-site	0	0	0	10,135	2,130
Cyclohexane					
Releases					
Fugitive air	132,000	66,000	47,000	8,300	51,000
Stack air	1,300	1,000	870	650	1,100
Land	7	87,000	0	0	0
Transfers					
Off-site	16	653	399	3,293	651
1,2-Dibromoethane					
Transfers					
Off-site	220	0	0	0	NR
1,2-Dichloroethane					
Releases	0	0	0	0	NR
Diethanolamine					
Releases					
Water	59,000	240,000	9,800	0	0
Transfers					
Off-site	9	64	13	29	0
Ethylbenzene					
Releases					
Fugitive air	57,000	36,000	33,000	27,000	74,000
Stack air	3,800	3,700	4,200	9,800	9,000
Water	0	0	0	6	1
Land	4	40,000	0	0	0
Transfers					
Off-site	770	30,720	18,269	54,722	13,034
Ethylene					
Releases					
Fugitive air	50,000	36,000	34,000	22,000	25,000
Stack air	7,000	0	130	1,500	1,400

1 *NR = Not Reported*

Table 2 (continued)

Chemical	Quantity Released (pounds)				
	1988	1989	1990	1991	1992
Ethylene Glycol					
Releases	0	0	0	0	NR[1]
Glycol Ethers					
Releases	0	0	0	0	NR
Hydrochloric Acid					
Releases	0	0	0	0	NR
Lead					
Releases					
Water	0	0	0	23	NR
Land	1,200	0	0	0	
Transfers					
Off-site	750	0	0	0	
Manganese					
Releases	0	0	0	0	NR
Methanol					
Releases					
Fugitive air	21,000	0	0	0	NR
Land	7	0	0	0	
Transfers					
Off-site	2	0	0	0	
Methyl tert butyl ether					
Releases					
Fugitive air	0	0	0	12,000	21,000
Stack air	750	1,900	1,900	30,000	17,000
Water	0	0	0	4	0
Molybdenum trioxide					
Releases	0	0	0	0	0
Transfers					
Off-site	0	0	0	0	68,000
Napthalene					
Releases					
Fugitive air	0	0	0	3,800	4,000
Stack air	0	0	0	240	190
Water	0	0	0	3	0
Nickel					
Releases					
Stack air	250	0	0	0	NR
Land	13,000	0	0	0	
Transfers					
Off-site	440	0	0	0	

1 *NR = Not Reported*

Table 2 (continued)

Chemical	Quantity Released (pounds)				
	1988	1989	1990	1991	1992
Phenol					
Releases					
Fugitive air	0	0	0	2,800	3,400
Stack air	250	0	0	0	8
Water	0	510	580	50	79
Land	11	0	0	0	0
Transfers					
Off-site	3	9	4	14	0
Phenylenediamine					
Releases	0	0	0	0	NR[1]
Phosphoric Acid					
Releases					0
Propylene					
Releases					
Fugitive air	120,000	99,000	97,000	32,000	43,000
Stack air	14,000	1,500	130	1,200	1,200
Sodium hydroxide					
Releases	0	0	0	0	NR
Sulfuric acid					
Releases					
Stack air	10,000	6,200	0	0	16
Toluene					
Releases					
Fugitive air	260,000	170,000	160,000	110,000	300,000
Stack air	42,000	35,000	36,000	23,000	23,000
Land	74	140,000	0	0	0
Water	0	0	0	54	2
Transfers					
Off-site	560	23,000	13,840	56,085	13,838
1,1,1-Trichloroethane					
Releases					
Fugitive air	8,100	6,100	4,700	6,200	NR
Stack air	250	0	0	0	
Land	3	0	0	0	
Transfers					
Off-site	2,801	0	0	2	
1,2,4-trimethyl benzene					
Releases					
Fugitive air	31,000	28,000	27,000	15,000	29,000
Stack air	3,000	1,400	760	1,300	1,500
Land	7	24,000	0	0	0
Transfers					
Off-site	460	19,080	10,660	57,935	11,750

1 *NR = Not Reported*

Table 2 (continued)

Chemical	Quantity Released (pounds)				
	1988	1989	1990	1991	1992
Xylene					
Releases					
Fugitive air	100,000	80,000	76,000	87,000	210,000
Stack air	31,000	29,000	29,000	13,000	18,000
Land	7	190,000	0	0	0
Water	0	0	0	34	2
Transfers					
Off-site	1,390	59,400	34,580	86,037	21,451
Zinc					
Releases					
Fugitive air	3,700	3,400	3,400	3,200	2,900
Stack air	0	0	0	0	0
Water	670	664	675	613	4,800
Land	5,300	0	0	0	0
Transfers					
Off-site	2,360	7,160	7,120	6,014	5,489

- Shell fugitive air releases increased from 25,000 pounds in 1991 to 54,000 pounds in 1992. This increase was a result of new calculations used for determining air emissions at the wastewater treatment plant. Wastewater treatment plant influent concentration data was obtained during a 3-month pilot study conducted by Shell. Chemical concentrations were higher than previously reported and additional chemicals were identified in the wastewater. As a result, air emissions show an increase from 1991 to 1992 for the following chemicals:

- benzene	- cumene	- MTBE
- cresol	- cyclohexane	- 1,2,4-trimethyl benzene
- ethyl benzene	- toluene	- xylene

- Ammonia air stack emissions increased from 250 pounds in 1988 to 180,000 pounds in 1989. In 1989, Shell began injecting ammonia into the electrostatic precipitators (ESP) at the hydrocracking units to improve efficiency. Stack air emissions are based on the amount of ammonia purchased and injected into the ESPs.

- Benzene fugitive air emissions increased from 160,000 pounds in 1991 to 270,000 pounds in 1992. A new method for calculating benzene emissions from wastewater was used in 1992. Colleen Hutchings, Senior Engineer for Shell indicated that emissions for 1991 would be recalculated using the new information and reporting would be updated.

  Fugitive benzene emissions from the cooling towers were calculated to be over 94,000 pounds. Remediation groundwater extracted for use in the refinery cooling towers is contaminated with benzene. Several wells are used to extract the contaminated groundwater with benzene concentrations ranging from 0 to 52 ppm. Based on large flows (approximately 3,400 gallons per minute combined flow) the amount of benzene contained in the extracted water is 94,800 pounds. All the benzene is assumed to be released to the atmosphere.

Stack air emissions decreased from 74,000 pounds in 1989 to 55,000 pounds in 1990. This was primarily due to emission calculations used for storage tanks. Better equations for fitting losses were used in 1990. Sample calculations for storage tanks are presented in Appendix C. Shell also decreased gasoline shipments in 1990.

Stack air emissions decreased from 58,000 pounds in 1991 to 18,000 pounds in 1992. This is due to the installment of a vapor recovery system at the benzene barge loading area in March 1992. Benzene vapors generated during barge loading are vented to a flare. Flare emissions are calculated using factors instead of control efficiencies. Flare emission calculations are shown in Appendix D.

Benzene land releases increased from 110 pounds in 1988 to 33,000 pounds in 1989. This increase was the result of an on-site gasoline spill. The 1989 increase in land releases for ethyl benzene, 1,2,4-trimethyl benzene, toluene, and xylene are also a result of the gasoline spill.

Off-site transfers increased substantially from 1988 to present. In November 1988, Shell began shipping primary solids from the wastewater treatment plant off-site. Prior to that date, primary solids were land disposed on-site. Consequently, a decrease occurred in the land releases during this time. Off-site transfer increases for chromium, cyclohexane, diethanolamine, ethyl benzene, lead, toluene, 1,2,4-trimethyl benzene, xylene, and zinc are also a result of this change.

- Chlorine stack air emissions increased from zero pounds in 1991 to 1,100 pounds in 1992. The increase was caused by two accidental releases that occurred at the Aromatics unit.

- Cobalt compounds were not reported in 1990 because they reportedly did not exceed the 10,000 pound threshold. Cobalt compounds are present in the catalysts used in the hydrotreaters and the steam methane reformer (SMR). In 1990, the catalysts consisted of 2 to 4% cobalt compounds totaling approximately 7,600 pounds used at the SMR [Appendix E].

  Cobalt off-site transfers increased from zero pounds in 1991 to 14,840 pounds in 1992. Shell did not include catalysts sent off-site for recycling as an off-site transfer prior to 1992. Shell submitted an updated Form R in November 1993 [Appendix F].

- Shell reported copper compounds in 1987, 1989, and 1990. Copper compounds are present in the catalyst used in the SMR unit and in lubricant additives. In 1987, the catalyst in the SMR was replaced and the used catalyst was shipped off-site for recycling. In 1989 and 1990 the 10,000 pound threshold level was exceeded by the copper contained in the lubricant additives. In 1988, the threshold value was not exceeded, therefore, a Form R was not submitted.

- Cumene releases showed a reduction from 260 pounds in 1990 to 110 pounds in 1991. 1990 values were based on estimates and 1991 values were based on actual usage (purchase records). The use of cumene has been discontinued since 1991 and, therefore, will not be reported on future Form Rs.

  Cumene off-site transfers increased from zero pounds in 1990 to 10,135 pounds in 1991. Start-up of the major effluent treatment project (MEP) generated slop oil emulsion containing cumene.

  Cumene transfers off-site decreased from 10,135 pounds in 1991 to 2,130 pounds in 1992. The decrease is due to the installation of a more efficient pump at the DAF unit, which generates less slop oil emulsions. Off-site transfers of cyclohexane, ethylbenzene, toluene, 1,2,4-trimethyl benzene, and xylene also decreased.

- Cyclohexane fugitive air releases increased from 25,000 pounds in 1987 to 132,000 pounds in 1988. This increase is a result of Shell using a new calculation method for the primary oil/water separator (master box) emissions. In 1989, the fugitive air releases decreased 50% because the master box was covered.

  Fugitive air releases decreased from 47,000 pounds in 1990 to 8,300 pounds in 1991. The master box was removed from service

  and replaced with new CPI separators that are vented to a flare. Installation of this equipment was part of the MEP.

- Lead compounds did not exceed the reporting threshold in 1992, therefore, Shell did not submit a Form R. Shell last produced leaded aviation gasoline in 1991.

- MTBE fugitive emissions increased from 12,000 pounds in 1991 to 21,000 pounds in 1992. This is due to increased emissions from cooling towers caused by an increase in makeup water from the North Property well fields. Increased SARA chemical concentrations are present in the makeup water.

- Molybdenum trioxide off-site transfers increased from zero pounds in 1991 to 68,000 pounds in 1992. Shell did not include catalysts sent off-site for recycling as an off-site transfer prior to 1992. Shell submitted an updated Form R in November 1993 [Appendix G].

- Sulfuric acid off-site transfers have not been included on the 1991 and 1992 Form R submittal. Colleen Hutchings, Senior Engineer, stated that spent sulfuric acid is not a waste under the Resource Conservation and Recovery Act definition and, therefore, reporting is not necessary. Approximately 100,000 tons of sulfuric acid are transferred to an off-site facility for regeneration.

- 1,1,1-trichloroethane was not reported in 1992 because it did not exceed the reporting threshold. The fugitive emissions were 6,000 pounds in 1991. Shell indicated that use of this chemical is being phased out, and that no additional purchase orders will be placed.

SUMMARY OF FINDINGS

Based on inspection observations, discussions with Shell personnel, and review of documentation, the following areas of noncompliance of the EPCRA requirements were identified.

40 CFR § 302.6(a)	Shell's notifications to NRC for 12 reportable releases were not made immediately following the release.
40 CFR 355.40(b)(1)	The state emergency response commission and the local emergency planning committee were not immediately notified of 12 reportable releases.
40 CFR § 372.30(a)	Shell failed to report approximately 15,000 pounds of cobalt transferred off-site for disposal or recycling during 1990.
	Shell failed to report approximately 68,000 pounds of molybdenum trioxide transferred off-site for disposal or recycling during 1990.
	Shell failed to report sulfuric acid transferred off-site in 1991 and 1992. Approximately 100,000 tons of sulfuric acid are annually transferred off-site for recycling.

AREAS OF CONCERN*

- Shell does not report all releases above the reportable quantity. The 1,000 ppm SO_2 emission limit for the sulfur recovery unit (SRU) was

* *Areas of concern are inspection observations of potential problems that could result in noncompliance with permit or regulatory requirements, or are areas associated with pollution prevention issues.*

exceeded on 28 occasions from February 1991 through October 1993. During the excess emissions, the quantity of SO_2 released ranged from 25 pounds to 1,576 long tons. The operating permit for the SRU allows excess emissions provided that the Illinois Environmental Protection Agency is notified immediately. Shell considers these incidents permitted releases and does not report them to the state and local emergency committees.

- Fugitive benzene emissions from the cooling towers were calculated to be over 94,000 pounds. Remediation groundwater extracted for use in the refinery cooling towers is contaminated with benzene. Several wells are used to extract the contaminated groundwater with benzene concentrations ranging from 0 to 52 ppm. Based on large flows (approximately 3,400 gpm combined flow) the amount of benzene contained in the extracted water is 94,800 pounds. All the benzene is assumed to be released to the atmosphere.

TOXIC SUBSTANCES CONTROL ACT

MULTI-MEDIA COMPLIANCE INVESTIGATION

Shell Oil Company
Wood River Manufacturing Complex
Roxana, Illinois

<u>Facility Address</u>

Shell Oil Company
Wood River Manufacturing Complex
Highway 111
Roxana, Illinois 62084
(618) 255-2478

<u>Investigation Dates</u>

October 25 through November 5, 1993

<u>Lead Investigator</u>

Sergio Siao, Chemical Engineer
NEIC

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MEDIA REPORT

At the request of EPA Region 5, NEIC conducted a multi-media compliance investigation of the Shell Oil Company - Wood River Manufacturing Complex (Shell) located in Roxana, Illinois. This report, one of a series that addresses investigation findings, discusses Toxic Substances Control Act (TSCA) polychlorinated biphenyl (PCB) issues, and compliance at Shell.

REGULATORY SUMMARY

The Shell facility has no known PCB or PCB-contaminated equipment in operation. Thirteen indoor askarel transformers were removed over a 3-year period and disposed of in 1986, 1987, and 1988. Thirty-six PCB or PCB-contaminated transformers were retrofilled in 1986 and 1987. On January 18, 1991, EPA Region 5 and Illinois EPA jointly conducted a TSCA compliance inspection. Three field citations of noncompliance were issued for:

- Three PCB transformers (retrofilled in 1987) were not properly reclassified as non-PCB equipment.
- The same three transformers were not marked with M_L labels.
- The 1987, 1988, and 1989 annual documents did not list the three transformers as "In Service."

Based on data submitted by Shell and evaluation of the inspection report, EPA Region 5 (September 25, 1991) determined that each violation has been corrected.

ON-SITE INSPECTION SUMMARY

Credentials were presented to Joe N. Brewster, Manager, Environmental Conservation for Shell. Following a general discussion of the complex operations, organization, safety and environmental programs, a plant tour was conducted. TSCA inspection forms were discussed with and signed by Jay D. Rankin, Senior Engineer, Environmental Conservation, prior to the on-site PCB inspection [Appendix A]. Exit conferences between regulatory and refinery personnel [Appendix B] were conducted to discuss preliminary inspection findings. NEIC personnel stressed that final determinations will be made in conjunction with regional and state personnel.

The complex has no PCB transformers or PCB capacitors in service. A review of the facility's annual reports for the past 3 years (1990, 1991, and 1992) [Appendix C] indicated that no PCB transformers or PCB capacitors have been in service since January 1, 1991. During the NEIC on-site inspection several transformers were inspected and the labels indicated that they did not contain PCBs. Photographs of the inspected transformers are contained in Appendix D.

The facility provided an inventory of the hydraulic equipment and heat transfer systems [Appendix E]. Most of the hydraulic equipment was tested for PCBs in 1986 and found to contain less than 1 part per million (ppm) PCB. Three heat transfer systems in the alkylation/benzene extraction unit have been in service since 1942, 1943, and 1953, and have not been tested for PCBs. Whenever there is a shut down for maintenance of the unit, the heating media has either been replenished with make-up oil or replaced with fresh oil.

COMPLIANCE STATUS

Based on inspection observations, discussions with Shell personnel, and review of documentation, there were no areas of noncompliance noted during the inspection.

One area of concern was identified during the NEIC investigation. Areas of concern are inspection observations of potential problems that could result in noncompliance with permit or regulatory requirements, or are areas associated with pollution prevention issues.

- Shell has not tested the heat transfer systems at the alkylation/benzene extraction unit for PCBs.

LABORATORY EVALUATION

MULTI-MEDIA COMPLIANCE INVESTIGATION

Shell Oil Company
Wood River Manufacturing Complex
Roxana, Illinois

Facility Address

Shell Oil Company
Wood River Manufacturing Complex
Highway 111
Roxana, Illinois 62084
(618) 255-2478

Investigation Dates

November 2 through 4, 1993

Lead Investigator

Jim Seidel, Chemist
Willis Collins, Chemist
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LABORATORY REPORT

At the request of EPA Region 5, NEIC conducted a multi-media compliance investigation of the Shell Oil Company - Wood River Manufacturing Complex (Shell) in Roxana, Illinois. This report, one of a series that addresses investigation findings, discusses laboratory evaluation and compliance at Shell.

REGULATORY SUMMARY

Shell operates analytical equipment and laboratories to monitor analytes important in maintaining compliance with a number of media regulations. Shell reports data relating to water discharges regulated under National Pollution Discharge Elimination System (NPDES) Permit Number IL0000205; monitors sulfur levels in refinery pitch regulated under various air permits; and has monitored benzene levels from wastewater, as required by 40 CFR Part 61 Subpart FF.

LABORATORY INSPECTION SUMMARY

Credentials were presented to Joe Brewster, Manager, Environmental Conservation, Shell. A briefing of safety procedures and requirements was conducted by Robert Miller, process chemist assigned to Environmental Conservation, Shell. A tour of the relevant laboratory facilities was conducted and the following areas inspected: The NPDES permitted wastewater treatment plant and related sampling points; sample storage area; and laboratory areas conducting tests for NPDES permitted parameters, sulfur content in refinery pitch, and benzene, toluene, ethylbenzene, and xylenes (BTEX) in wastewater. During the inspection, laboratory procedures were observed for analyzing total sulfur in refinery pitch; BTEX in wastewater; as well as the following NPDES permit parameters: pH, biochemical oxygen demand (BOD_5), total dissolved solids (TDS), oil and grease, phenols, ammonia, sulfides, and hexavalent chromium. Discussions concerning the procedures for determining the NPDES permitted parameters of total cyanide, sulfate, chlorides, and total chromium were conducted with the appropriate Shell analysts. Records/documents affiliated with these activities were also reviewed. Exit conferences between regulatory and refinery personnel [Appendix] were conducted to discuss preliminary inspection findings. NEIC personnel stressed that final determinations will be made in conjunction with regional and state personnel.

Sample Collection, Storage, and Handling

Grab sampling for NPDES discharge point 002 (clarifier outfall, Special Conditions 5A and B of NPDES Permit Number IL0000205) was observed. Samples are collected in one-half gallon plastic bottles, with the exception of pH (1-liter plastic bottles), and oil and grease (three 8-ounce glass jars). The preservative in each bottle, if any, is determined by the test to be performed and is documented in the Shell laboratory standard operating procedure (SOP) manual. Based on Shell's SOP manual and on-site observations, inappropriate containers or chemical preservatives were used with samples for the NPDES permitted testing of phenols, sulfides, and hexavalent chromium levels, as follows.

- The sample collection bottle used for phenols analysis is not appropriate. Shell uses a one-half gallon plastic bottle. The *Standard Method* test being used and 40 CFR § 136.3 states that only glass containers are acceptable. The use of plastic containers may bias the test results high or low if phenols are leached from, or adsorbed onto the plastic.

- The chemical preservative used in samples to be analyzed for sulfides is not appropriate. Shell uses 2 mL of a zinc acetate solution as a preservative. 40 CFR § 136.3 states that both zinc acetate and sodium hydroxide (to give a pH > 9) are to be used. Without the use of sodium hydroxide, sulfides may be lost, resulting in under reporting of sulfide levels.

- The chemical preservative used in samples to be analyzed for hexavalent chromium is not appropriate. Shell uses 5 mL of a 50% sulfuric acid solution. 40 CFR § 136.3 states that no chemical preservative is to be used. The use of sulfuric acid enhances the potential that hexavalent chromium will be reduced to trivalent chromium, resulting in under reporting of hexavalent chromium levels.

On-site observations and records revealed that the samples collected for determining phenols, sulfides, hexavalent chromium, total chromium, oil and grease, BOD_5, chemical oxygen demand (COD), ammonia, and total cyanide were not stored at the required temperature of 4 °C. Shell's temperature records showed that the sample storage cooler's temperature varied between 3 °C and 15 °C within a 1-month period from August 20 to September 23, 1993. In addition, samples being prepared for analysis were observed standing throughout the day in laboratory environments reaching temperatures of approximately 29 °C. Lack of rigorous temperature control may lead to undesirable changes in analyte levels resulting in under or over reporting of the true analyte levels.

Test Methods

On-site observations and records revealed that the required tests were being run for the NPDES permitted parameters; however, some of the tests were inappropriately conducted as follows.

- Shell's BOD_5 incubator does not always maintain a temperature of 20 °C ± 1 °C, as specified in *Standard Method* 5210, resulting in BOD_5 values which may over or under report the true value. In addition, an uncalibrated thermometer was being used to report the incubator temperature even though a properly calibrated (NIST) thermometer was inside the incubator. The difference between the uncalibrated and calibrated thermometers was 0.7 °C. Shell personnel were unaware of the fact that the thermometer used to report incubator temperatures was not calibrated and that a calibrated thermometer was available.

- The test used for ammonia determinations (*Standard Method* 4500-NH_3 G) is not properly conducted. The test requires distillation (*Standard Method* 4500-NH_3 B) prior to measurement, and Shell did not do the distillation. Because the potential presence of oils in the test materials could impede ion transport across the selective membrane, lack of the distillation step is likely to yield ammonia values which under report the true value.

- pH determinations reported on Shell's monthly DMRs are not performed immediately, as required by 40 CFR § 136.3. On November 3, 1993, the grab samples for the permitted sampling points were analyzed at approximately 1000 hours. The exact time of sampling was unknown to the analyst. However, Shell's protocol required the grab samples to be taken before 2400 hours on November 2, 1993, so they could be dropped off at the laboratory for analysis on November 3, 1993. This translates into at least a 10-hour delay between sampling and analysis. Shell's current protocol also necessitated refrigerating the samples. As a result, the analyst heated uncovered aliquots of the samples in a 103 °C oven before obtaining the reported measurement. Such manipulation may affect the pH of the sample.

- A review of laboratory records indicated that the total chromium determinations for January 1991 were not conducted in accordance with Shell's SOP and EPA Method 200.7.

    - Only one calibration blank was determined, rather than the minimum of a calibration blank at the beginning and end of each analysis run.

    - The calibration blank contained chromium levels near, or in excess of those reported for the samples. In such a case, the results should have been blank corrected or the analysis performed again.

    - The required procedure for determining the method detection limit was not being followed and there were no records indicating that it had been done for the last 3 years.

General Laboratory Practices

While Shell does have a quality assurance (QA)/quality control (QC) program, some aspects of it are not being completely implemented, and Shell's program lacks some aspects of common QA/QC procedures. The end result is the inability to know the quality of the data being produced on a day-to-day basis.

Sample Collection

Individual sample containers collected by the treatment plant operator(s) lacked unique identification. Each of the sample containers were labeled only as to the type of preservative/test. The eight sample containers making up a sampling event were placed into two carriers having only a piece of yellow tape with the day of the week as identification. A single Shell identification tag was attached to one of the carriers. The time of collection and who collected the sample was not indicated on any of the samples.

Chain-of-custody procedures were not followed and samples were stored in an unsecured cooler outside of the laboratory building.

Laboratory and Sampling Glassware

Written SOPs for the cleaning of laboratory glassware were not followed.

- The one-half gallon plastic sample collection containers were visibly discolored and, when wiped on the interior, yielded obvious dirt and grime. Cleaning of the containers was observed on November 2 and 3, 1993 and consisted of simply rinsing the containers with tap water.

- The separatory funnels used for determining oil and grease were only rinsed with distilled water. The funnels were visibly discolored with brown, oily material, especially around the stopcock.

- Glassware, including distillation apparatus crucial to required testing, that was not washed in the automatic dishwasher was simply rinsed with tap or distilled water and placed back into service.

Standards

A record of the preparation of standards is not kept. At the time of inspection, most of the working standards were dated "10/27/93." Neither the laboratory manager nor the analyst could prove what the schedule was over the past 3 years for replacement of standards, or the source and batch/lot of the reagents used to prepare standards.

Only a single standard is prepared, diluted as needed, and then used to calibrate, check calibration, and spike samples. At a minimum, an independent standard (prepared separately from a different source and/or batch/lot) should be used to check calibration and verify the working standard was prepared properly.

Calibration

Daily calibration checks are not performed for several tests. Calibration checks for the spectrometers used in determining phenols, sulfides, and hexavalent chromium levels were not being performed, and no calibration check was conducted on the pH meter.

Instrument calibration curves were not produced on a regular basis. The calibration curve for the spectrometer used in determining phenols and sulfides levels was redone approximately every 15 months, even though numerous instrument maintenance procedures, such as bulb replacement, had occurred during this time. Similar conditions existed for the spectrometer used for hexavalent chromium determinations.

Blanks

Method blanks were not being run through the test procedure. The only record of appropriate method blank test results were obtained in July 1993. The laboratory manager indicated that this was the first time a method blank had been obtained and recorded for most tests.

Limit of Detection

No records exist for the determination of the limit of detection (LOD) for the tests being performed, and laboratory personnel indicated that LODs are not determined. Shell has no proof that the results they are reporting are above or below their actual and consistently achievable LODs.

Inadequate Execution of the Concept of Batch QC

Shell analysts do not perform duplicate analysis and spikes on the same samples. Procedures are not in place that indicate what to do in the event a batch fails QC requirements.

No Procedure for Denoting Suspect Test Results

No procedure is in place for flagging, or denoting, test results which failed some critical element required by the test method. For example, BOD_5 data from in-house testing was averaged with those of the contract laboratory and reported on the monthly DMR for January 1993, even though the incubator temperature was not maintained at 20 °C ± 1 °C.

Problems with Shared Equipment

Potential problems with equipment used for NPDES and process testing occurs primarily when electrodes susceptible to coating by oils are used. For example, the pH measurement recorded on November 3, 1993 for the monthly DMR was performed immediately after measuring the pH of a "slop tank" sample containing oils. The pH probe was rinsed only with distilled water before the NPDES permitted pH measurement was recorded. When a glass pH electrode is coated with oil, the interaction of hydrogen ions with the glass surface is impeded, resulting in incorrect pH values.

SUMMARY OF FINDINGS

AREAS OF NONCOMPLIANCE

Based upon inspection observations, discussions with Shell personnel, and review of documentation, the following areas of noncompliance were noted:

40 CFR § 136.3	Inappropriate containers or chemical preservatives were being used for samples analyzed to determine compliance with the NPDES permitted levels for phenols, sulfides, and hexavalent chromium.
40 CFR § 136.3	Samples collected for analysis by NPDES permitted tests, including samples of phenols, sulfides, hexavalent chromium, total chromium, oil and grease, BOD_5, COD, ammonia, and total cyanide were not being stored at the required temperature of 4 °C.
40 CFR § 136.3	pH determinations are not performed immediately after taking the sample.
Standard Method 5210, as referenced in 40 CFR § 136.3	The BOD_5 incubator does not maintain the temperature at 20 °C ± 1 °C.
Standard Method 4500-NH_3 G, as referenced in 40 CFR § 136.3	The ammonia determination is not properly conducted. The lab does not use *Standard Method* 4500-NH_3 B prior to measurement with *Standard Method* 4500-NH_3 G.
40 CFR § 136, Appendix B and 40 CFR § 136, Appendix C, Section 12	Method 200.7 for the determination of total chromium was not followed; an insufficient number of calibration blanks was performed and the procedure for determination of the method limit of detection was not performed.

AREAS OF CONCERN

Based upon inspection observations, discussions with Shell personnel, and review of documentation, the following areas of concern* were noted.

- The Shell laboratory QA/QC program for analyzing NPDES permitted parameters is inadequate in the following areas:

  - Individual sample containers collected by the treatment plant operator(s) lacked unique identification.
  - Sample chain-of-custody procedures were incompletely followed.
  - Written SOPs for the cleaning of laboratory glassware were not followed.
  - A record of the preparation of standards is not kept.
  - Only a single standard is prepared, diluted as needed, and then used to calibrate, check calibration, and spike samples.
  - Daily calibration checks are not performed for most tests.
  - Instrument calibration curves were not produced on a sufficiently regular basis.
  - Analytical method blanks are not being performed.
  - No records exist for the determination of the LOD for the tests being performed.
  - Execution of the concept of batch QC is inadequate.
  - No procedure is available for denoting suspect test results.
  - Potential problems exist with shared usage of equipment.

* *Areas of concern are inspection observations of potential problems that could result in noncompliance with permit or regulatory requirements, or are areas associated with pollution prevention issues.*